

*KABACHNIK, M.I.*

USSR/Organic Chemistry. Synthetic Organic Chemistry.

G-2

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11372.

Author : Kabachnik, M. I. and Rossiyskaya, P. A.

Inst : Academy of Sciences USSR *Insr. Organoelemental Compounds.*

Title : Reactions of Chloroacetyl Chloride, Trichloroacetyl Chloride, and Phosgene with Trialkyl Phosphites.

Orig Pub: Izvest Akad Nauk SSSR, Otdel Khim Nauk, No 1, 48-53 (1957)

Abstract: The reaction of  $\text{COCl}_2$  with  $(\text{RO})_3\text{P}$  (I) ( $\text{R} = \text{CH}_3$ ) gives  $\text{ClCOP(O)(OCH}_3)_2$  (II), which on reaction with I ( $\text{R} = \text{CH}_3$ ) yields  $[\text{CH}_2\text{O}_2\text{P(O)}]_2\text{CO}$  (III),  $\text{ClCH}_2\text{COCl}$  (IV) and  $\text{Cl}_3\text{CCOCl}$  (V) with I give vinyl esters  $(\text{RO})_2\text{P(O)C}(-\text{CH}_2\text{O}_2\text{P(O)(OR)}_2$  (VI). A discussion of the reaction mechanism is given. Preparation: 37.2 gms I ( $\text{R} = \text{CH}_3$ ) are saturated (cooling) with dry  $\text{COCl}_2$ ; when the reaction is completed, the reaction mixture is

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*KABACHNIK, M. I.*

USSR/General Problems. Methodology, History, Scientific Institutions  
and Conferences, Instruction, Questions Concerning Bibli-  
graphy and Scientific Documentation.

A

Abs Jour: Referat. Zhurnal Khimiya, No 2, 1958, 3468

Author : M.I. Kabachnik.

Inst :

Title : Academician Aleksandr Yerminigel'dovich Arbuzov.

Orig Pub: Khim. nauka i prom-st', 1957, 2, No 4, 493-496.

Abstract: To the 80th anniversary of his birthday. See also RZhKhim, 1958,  
11, 12.

Card : 1/1

-19-

**"APPROVED FOR RELEASE: 08/10/2001**

**CIA-RDP86-00513R000619720013-2**

## Methodological principles of the study of differentiation

1. E. d.  
E. d.

**APPROVED FOR RELEASE: 08/10/2001**

CIA-RDP86-00513R000619720013-2"

AUTHORS: Medved', T. Ya., Kabachnik, M. I.

62-11-9/29

TITLE: Synthesis of Aminoalkylphosphonic Acids (Sintez aminokilfosfitovykh kislot) Reaction of Some Heterocyclic Ketones with Dialkylphosphites and Ammonia (Reaktsiya nekotorykh geterotsiklicheskikh ketonov s dialkifosfitami i ammiakom)PERIODICAL: Izvestiya AN SSSR, Otdelenie Khimicheskikh Nauk, 1957, Nr 11, pp. 1357-1362 (USSR)ABSTRACT: Here is demonstrated that the reaction discovered earlier (reference 1) for production of ether of the aminoalkylphosphonic acids under the influence of ammonia can be extended on the mixture of dialkylphosphite and aldehyde or ketone, also on the case of the heterocyclic ketones. As initial matters 1.2.5-trimethyl-4-piperidone, which by the paper of Nazarov and Rudenko (reference 2) at present has become an easily accessible product as well as the 2.2-dimethyl-tetrahydropyran-4-on have been applied. The ethers of the aminophosphinic acids of piperidone-and tetrahydropyran series and some of their derivatives were obtained. For explaining the influence of the acyl-amino-group on the physiological activity of the matters obtained, the ethers of the respective acyloxyphosphinic acid were produced synthetically. For this purpose the reaction of Abramov (reference 4)

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*KABACHNIK M.I.*  
KABACHNIK, M.I.; IOFFE, S.T.; VATSURO, K.V.

Cis-trans-enol tautomerism. Ukr. khim. zhur. 23 no. 5:602-614 '57.

1. Insitut elementoorganicheskikh soyedineniy AN SSSR.  
(MLRA 10:11)  
(Tautomerism)

Kabachnik, M. I.

74-11-3/7

AUTHORS: Nesmeyanov, A. N. , and Kabachnik, M. I. (Moscow)

TITLE: The Organic Chemistry of the USSR Since 40 Years (Sovetskaya orga-nicheskaya khimiya za 40 let)

PERIODICAL: Uspekhi Khimii, 1957, Vol. 26, Nr 11, pp. 1241 - 1294 (USSR)

ABSTRACT: Although chemists like Mendeleev and Butlerov took an active part in the structure of organic chemistry in pre-revolutionary Russia, the Soviet-Union had to perform an immense, wide-ranging work for its further development both theoretically and practically. The attained successes are entirely due to the activity of the scientific and technical institutes. The jubilee articles contain the most important and also practically utilized synthesis . The increasing utilization of both physical and physico-chemical methods of investigation of organic compounds and reactions, are a characteristic feature of the last decades. The frequent application of all sorts of optical spectroscopy of X-ray structure analysis, of dielectrical, magnetical and radiospectroscopical methods of X-ray spectra plays an important rôle. The elaborate studies of B. K. Syrkin and his students were devoted to the investigation of the fine structure of the organic molecules. Zavoykiy discovered recently the method of paramagnetic resonance. The analysis of struc-

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KABACHNIK, M.I.

PA - 2503

AUTHOR:

POTKOV, L.L.

TITLE:

Scientific Meetings and Conferences. (Nauchnye sessii konferent-sii scveshchaniya, Russian)  
Vestnik Akademii Nauk SSSR, 1957, Vol 27, Nr 2, pp 102 - 106

PERIODICAL:

(U.S.S.R.)

Received: 5 / 1957

Reviewed: 6 / 1957

ABSTRACT:

From October 29th to 31th a conference was held in Kiev of the Scientific Council of the Department for Chemistry of the Academy of Science of the U.S.S.R., of the Department for Geological Sciences of the Academy of Science of the Ukrainian SSR and the Kiev Department of the Soviet Chemical Society on problems of stereochemistry of chemical reactions. A.A. Nesmeyanov read a paper on his own behalf as well as on the behalf of A.E. Borisov on the stereochemistry of olefinic hydrocarbon compounds. The paper contained the results of investigations of stereometric and metalorganic compounds of the ethylene series. These investigations enabled the authors to deduce a law, according to which homolytic replacements of olefinic carbon atoms occur in such a way, that the geometrical configuration remains unchanged.

This theorem was examined on the basis of the organic compounds of Sb, Li, Tl. On this occasion the investigation considered not only compounds originating from the active force of non-metallic halides, for example  $HgCl_2SbCl_5$ , but also acetous metal compounds.

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## Scientific Meetings and Conferences.

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The reviewer checked the work of the American authors I.Braude, Dreiding, Kurtin, Jonson, Steiner. The discussion group (E.A. Zhilov, M.I.Kabachnik) emphasized the importance of the theorem on the perseveration of the configuration in olefines in the case of atomic changes or changes of atom groups respectively, if double combination is considered.

The reviewer Zhilov made a report on the mechanism of the Cis-compound. He underlined that markedly polar reactions occur as a condition for the formation of Cis-compounds.

M.I.Kabachnik read a paper on the tautomeric properties of cis- and trans-states on his own behalf and on the behalf of S.T.Joffe and K.V.Vatsuro. Investigations of the dependence of the constants of the tautomeric equilibrium of ketoenoles showed, that these ketoenoles form cis-enoles. It was determined that the enolisation of trans-fixed enoles is independent of the nature of the solvent. Their enolisation corresponds to the general formula. With the help of these ascertainties, the contents of the two stereometric forms in the solution can be calculated.

E.A.Zhilov pointed to the fact that on the occasion of studying the stereochemistry of the acetylene compounds the fact must be considered, that acetylene in its active state either constitutes a trans-state or in the case of greater efficiency a cis-state,

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Scientific Meetings and Conferences.

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which circumstance causes the formation of different ethylene branches.

Investigations in the field of kinetics (M.B.Neumann) and stereo-chemistry may be very helpful in the utilisation of high pressures.

The formation of trans-compounds was discussed by L.D.Bergelson, who maintained, that their formation is explained primarily by the geometry of molecules, not by the character of the reaction, as was imagined by E.A.Zhilov.

A.P.Terentiev reported on the problem of absolute asymmetric synthesis. During 1929 - 1930 optical active substances were obtained with the help of circular polarized light from the re-

actions of bromide and propionic acid.

Moreover, numerous other lectures were held, which cannot be dealt with in detail here.

ASSOCIATION: Not given

PRESENTED BY:

SUBMITTED:

AVAILABLE: Library of Congress.

Card 3/3

20-114-3-25/60

AUTHORS: Gefter, Ye. L., Kabachnik, M. I., Corresponding Member of  
the AN USSR

TITLE: The Production and Investigation of Some Vinyl Ethers of the  
Acids of Phosphorus (Sintez i issledovaniye vinylovykh  
efirov kislot fosfora)

PERIODICAL: Doklady Akademii Nauk SSSR, 1957, Vol. 114, Nr. 3, pp. 541-544 (USSR)

ABSTRACT: The not substituted vinyl ethers which recently became known  
were for the first time synthesized by the dehydrochlorina-  
tion of corresponding  $\beta$ -chlorethylic ethers. Somewhat later  
this was carried out by the interaction between acids of the  
trivalent phosphorus and chloracetaldehyde according to Perkow.  
In the present paper a new method of synthesizing vinyl ethers  
of phosphorus acids is described which is based on the inter-  
action between the chloranhydrides of these acids and acet-  
aldehyde and triethylamine. In this case the authors proceed-  
ed from the following assumptions: - Kabachnik and Shepeleva,  
when studying the reaction of the chloranhydrides of the acids  
of the trivalent phosphorus, came to the conclusion that this

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20-114-3-25/60

The Production and Investigation of Some Vinyl Ethers of the Acids of Phosphorus

of linear construction that is of ethers with only one double binding are formed. The ethers with 2 and 3 double bindings can be polymerized much more quickly. On this occasion spatially net-like polymers are formed which are insoluble in organic solvents. There are 2 tables and 10 references, 7 of which are Slavic.

ASSOCIATION: Scientific Research Institute for Plastic Substances and Institute for Elementary-Organic Compounds of the AN USSR (Nauchno-issledovatel'skiy institut plasticheskikh mass i Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)

SUBMITTED: February 7, 1957

Card 3/3

AUTHORS: Kabachnik, M. I., Corresponding Member of the 20-114-4-28/63  
Academy, Gilyarov, V. A.

TITLE: On Imides of Phosphorus Acids (Ob imidakh kislot). The Di-  
alkylphosphoryl-N-Phenyltriazenes and Their Salts (Dialkyl-  
fosforil-N-feniltriazeny i ikh soli)

PERIODICAL: Doklady Akademii Nauk SSSR, 1957, Vol. 114, Nr 4,  
pp. 781-784 (USSR)

ABSTRACT: In previous papers the authors had shown that the full ethers  
of the acids of 3-valent phosphorus enter into reaction with  
phenylazide and form imidophosphates. This reaction was pro-  
posed as characteristic of the derivatives of the said acids.  
It was of interest to study these reactions with the salts of  
the dialkylphosphites. According to several publications the  
phosphorus in them is 3-valent. The authors found that the  
free dialkyls do not react with phenylazide. Their salts how-  
ever (triethylammonium and sodium salts) enter into reaction  
and form salts of the dialkyl-N-phenylphosphoryltriazenes.  
From these free dialkylphosphoryl-N-phenyltriazenes may be  
isolated, which are representatives of a new class of phosphor-  
nitrogen compounds. The formation of these salts may serve as

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KABACHNIK, M.I.

20-3-25/59

AUTHORS Kabachnik, M.I., Corresponding Member AN URSR  
TITLE On the Tautomerism of Diphenylphosphite.  
(O tautomerii difenilfosfita - Russian)  
PERIODICAL Doklady Akademii Nauk SSSR, 1957, Vol 115, Nr 3, pp 512-515 (U.S.S.R.)  
ABSTRACT The tautomerism of the dialkylphosphites was several times investigated. It can be considered as an established fact that the position of equilibrium of this tautomeric system is to a great extent shifted in the direction of the model I (scheme given). The free dialkylphosphites show no properties characteristic of the compounds of the trivalent phosphorus, above all they do not enter into a combination reaction in the free electron couple of the phosphorus of the model II. This is also the case in solutions with the exception of highly basic media such as the tertiary amines. In such solutions, besides the undissociated molecules of dialkylphosphites, salts of the type:  $[\text{RO}_2\text{P}(\text{O}^-)\text{F}] [\text{HN}^+\text{R}_2]$  are contained the anion of which easily attacks sulphur and phenylacid. Dialkylphosphites adsorb sulphur relatively easily also in the dioxan medium in which the model II can be stabilized by a hydrogen binding. All indications tend to show that the equilibrium of the dialkylphosphites is shifted in the direction of model I and that the influence of certain exterior factors is necessary in order to cause the system to show the properties of the compounds of the trivalent phosphorus. If the tautomeric equilibrium of the dialkylphosphites is considered as an acid-basic protoptic one which was shifted in the direction of model I the relation of the acidity constants

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On the Tautomerism of Diphenylphosphite.

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on the occasion of the transition to the analogues of the dialkylphosphites can be changed by a corresponding modification of structure of the molecule. Thus systems with a different state of the tautomeric equilibrium can be produced. It was the authors' task to find such an effect, maintaining the diaden binding-system characteristic of the dialkylphosphites. They obtained diphenylphosphite with a quantitative yield by a careful saponification of diphenylchlorophosphite by an equivalent quantity of water on which occasion hydrochloric acid and the solvent were later removed in the vacuum. The authors moreover found out that diphenylphosphite enters into the following characteristic reaction at the free electron couple of the trivalent phosphorus: connection of phenylacid, connection of sulphur and chlorine copper. Finally the reaction of the diphenylphosphite with diazomethane is described. The obtained diphenylmethylphosphite was discovered by the reaction in the hydroxyl-group, in contrast to the above mentioned reactions.

There is 1 figure and 11 Slavic references.

ASSOCIATION Institute for Organic-Elemental Compounds of the A.N. of the AN USSR.  
(Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)  
SUBMITTED March 22, 1957  
AVAILABLE Library of Congress.  
Card 2/2

AUTHORS: Kabachnik, M. I., Corresponding Member of the AS USSR, Tavetkov, Ye. N. 20-117-5 25/54

TITLE: A Method for the Synthesis of Alkylphosphinic Esters (Metod sinteza efirov alkilfosfinistykh kislot)

PERIODICAL: Doklady AN SSSR, 1957, Vol. 117, Nr 5, pp. 817-820 (USSR)

ABSTRACT: These ethers are comparatively not easily accessible substances. A review of their synthesis since 1952 is given and of the usual methods of synthesis with their criticism. The general method of synthesis described here of the ethers alkyl- and aryl phosphinic acids is based upon the effect of magnesium-organic compounds on dialkyl-chlorine-phosphites at  $-60^{\circ}$   $(RO)_2PCl + R'MgX \rightarrow (RO)_2PR' + MgXCl$ .

The carrying out of the reaction at low temperature facilitates a selective substitution of the dialkyl-chlorine-phosphites by alkyl- and aryl radicals without touching the alkoxy groups. The reaction direction is given. Yields, constants, and analytic data of the produced ethers are given in table 1. Bromine derivatives were used as haloid alkyls. Chlorine benzyl and iodine methyl form an exception. The produced ethers succumb in air easily to an oxydation,

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A Method for the Synthesis of Alkylphosphinic Esters

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furthermore they easily iodine copper and sulphur. In order to confirm the structure of the synthesized substances some ethers of the alkylthiophosphinic acids and complex compounds of the arylphosphinic ethers were produced from it with iodine copper by means of the usual methods (table 2). In the ethers of the alkylphosphinic acids the observed molecular refractions were constantly higher by an average of 0,41 than the calculated. For the ethers of the arylphosphinic acids an exaltation of an order of magnitude of 1,20 was found. There are 2 tables, and 14 references, 8 of which are Slavic.

ASSOCIATION: Institute for Elemental-organic Compounds of the AS USSR  
(Institut elementoorganicheskikh soyedineniy Akademii nauk  
SSSR)

SUBMITTED: July 20, 1957

Card 2/2

AUTHORS: Kabachnik, M. I., Ioffe, S. T. 62-58-5-16/27

TITLE: On the Investigation of Tautomerism in Aprotic Solvents  
(K izucheniyu tautomerii v aprotnykh sredakh)

PERIODICAL: Izvestiya Akademii Nauk SSSR Otdeleniye Khimicheskikh Nauk,  
1958, Nr 5, pp. 628 - 630 (USSR)

ABSTRACT: According to Gammet (Reference 1) a difference must be made between ionization and dissociation in solutions. According to Izmaylov (Reference 2) the process of acid-dissociation consists of the following equilibrium-reactions: The solvation of the neutral acid- molecule, the dissociation of the solvate with the formation of solvated ions and the association of these ions in ion-pairs. Already earlier a general potentiometric method for the determination of the constants of the tautomeric equilibrium in conducting media was worked out.. In the present report they describe the colorimetric method elaborated by them for the determination of the constants of protolysis in aprotic solvents with low dielectricity-constant. The neutralization-reaction of the acid in aprotic solvents with low dielectric constant leads to the formation of non-dissociated

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On the Investigation of Tautomerism in Aprotic Solvents 62-58-5-16/27

ion-pairs. The values  $n$  are practically equal to 1. The consideration of Brønsted's dependence makes the application of the constants of the protolysis for the determination of the constants of the tautomeric equilibrium possible. There are 2 figures, 1 table and 7 references, 3 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR  
( Institute for Elemental-organic Compounds AS USSR)

SUBMITTED: December 17, 1957

1. Organic solvents--Chemical reactions 2. Organic solvents  
--Analysis 3. Acid-base equilibrium--Analysis 4. Colorimetry--Appli-  
cations

Card 2/2

AUTHORS: Kabachnik, M. I., Medved', T. Ya., Kozlova, G. K., Balabukha, V. S., Senyavin, M. M., Tikhonova, L. I. SOV/62-58-9-8/26

TITLE: Synthesis and Testing of the Complex-Forming Properties of Several Organophosphorus Compounds (Sintez i ispytaniya kompleksoobrazuyushchey sposobnosti nekotorykh fosfororganicheskikh soyedineniy)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 9, pp 1070 - 1075 (USSR)

ABSTRACT: After the discovery that the diaminocarboxylic acid series is highly active in forming complex compounds the authors of this paper became interested in studying the complexing properties of some  $\alpha$ -aminoalkyl phosphinic acids and their derivatives. Only a few papers appear in the publications on this topic (Refs 3-6). The authors investigated the complexing properties of some aminoalkyl phosphinic acids which they had previously prepared as well as several ethylenediaminodiphosphinic acids. The investigations showed that in the reaction between

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Synthesis and Testing of the Complex-Forming Properties of Several Organophosphorus Compounds SOV/62-58-9-8/26

ethylenediamine and dialkyl phosphites and aldehydes (or ketones), esters of ethylenediaminodialkylphosphinic acids form. By saponifying these esters the free acids can be obtained. The complexing properties of the ethylenediaminodialkylphosphinic acids so prepared were tested chromatographically. Other aminoalkyl phosphinic acids previously prepared were also studied to determine their complexing properties. It was shown that the ethylenediaminodialkylphosphinic acids form stable complex compounds with ytterbium and yttrium. There are 2 tables and 7 references, 2 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-organic compounds, AS USSR)

SUBMITTED: February 14, 1957

Card 2/2

AUTHORS: Medved', T. Ya., Kabachnik, M. I. SOT/62-58-10-9/25

TITLE:  $\beta$ -Ethyl Mercapto Ethyl Phosphites and Some of Their Properties ( $\beta$ -etilmerkaptoetilfosfity i nekotoryye ikh svoystva)

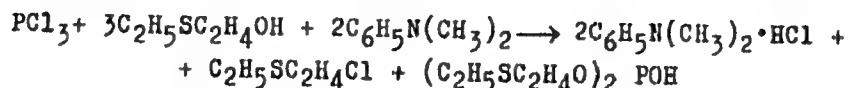
PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 10, pp 1212-1218 (USSR)

ABSTRACT: In connection with the investigation of the tautomerism of organophosphorus compounds it was of interest to investigate the synthesis as well as the properties of the esters of phosphoric acids which in the alkyl group contain the hetero atom in  $\beta$ -position. The authors selected the di- $\beta$ -ethyl mercapto ethyl phosphite to be the first one investigated of this type. They failed, however, in producing this compound under the conditions of the usual synthesis of dialkyl phosphites. The  $\beta$ -chloro-diethyl sulfide could be separated as the only reaction product. The synthesis of di- $\beta$ -ethyl mercapto ethyl phosphite could be realized only by the modification of the reaction according to the following equation:

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$\beta$  -Ethyl Mercapto Ethyl Phosphites and Some of  
Their Properties

SOV/62-58-10-9/25



Similar to this synthesis of di- $\beta$  -ethyl mercapto ethyl phosphite the ethyl- $\beta$  -ethyl mercapto ethyl phosphite could be produced. Some properties of the synthesized  $\beta$  -ethyl mercapto ethyl phosphite were investigated. The authors described the synthesis of tri- $\beta$  -ethyl mercapto ethyl phosphite. The di- $\beta$  -ethyl mercapto ethyl phosphite has the known properties of dialkyl phosphites. The di- $\beta$  -ethyl mercapto ethyl phosphite reacts with ketones and ammonia, with esters of the  $\alpha$  -amino alkyl phosphinic acids being formed. Di- $\beta$  -ethyl mercapto ethyl phosphite combines with aldehydes under the simultaneous formation of esters of the oxyalkyl phosphinic acid. In the regrouping of tri- $\beta$  -ethyl mercapto ethyl phosphite according to Arbuzov the di- $\beta$  -ethyl mercapto ethyl ester of the methyl phosphinic acid is formed (under the action of methyl iodide). There are 1 table and 9 references, 5 of which are Soviet.

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$\beta$  -Ethyl Mercapto Ethyl Phosphites and Some of  
Their Properties

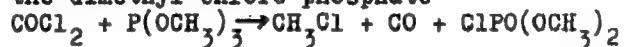
SOV/62-58-10-9/25

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk  
SSSR  
(Institute of Elementary Organic Compounds, Academy of  
Sciences, USSR)

SUBMITTED: March 12, 1957

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5(3)

AUTHORS: Kabachnik, M.I., Rossiyskaya, P.A. SOV/62-58-11-24/26TITLE: On the Reaction of Trialkyl Phosphites With Phosgene  
(O reaktsii trialkilfosfitov s fosgenom)PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958,  
Nr 11, pp 1398 - 1398 (USSR)ABSTRACT: This short report is a rectification of the article "On the  
Reaction of Chloro Acetyl Chloride, Trichloro Acetyl Chloride  
and Phosgene With Trialkyl Phosphites" published in this period-  
ical, Nr 1, 1957. The results described (Ref 1) could not be  
confirmed when the reaction was repeated. In a reaction of phos-  
gene with trimethyl phosphite apart from the separation of carbon  
monoxide the dimethyl-chloro phosphate

is formed. Since in this reaction the expected chloroformyl-phos-  
phinic ester was not obtained, the character of the following  
transformation products does not correspond to the formulae given  
in the same article and remains unexplained. There are 3 refer-  
ences, 1 of which is Soviet.

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5 (0)

CHICOM/5-58-12-14/25

AUTHOR: Kabaohnik, M. L., Member of AN SSSRTITLE: Study and Prospects of Phosphorus Organic High Polymers; A Scientific Report Submitted to Chung Kuo K'o Hsueh Yuan Hua Hsueh Yen Chiu So (Institute of Chemistry, Chinese Academy of Sciences) in October, 1958PERIODICAL: Hua Hsueh T'ung Pao, 1958, Nr 12, pp 696-700

ABSTRACT: The author introduces phosphorus high polymers by grouping them into carbon-chain polymers and heterochain polymers. The former are subdivided into two types: one has phosphorus atoms linked to the main carbon chains either directly or by hydrocarbon radicals.

$\text{CH}_2=\text{CH-PO(OR)}_2$  is the most important structural unit of this type. Polymers of this type with a practical use are ion-exchange resins which, however, are not synthesized by polymerization of phosphorus-containing monomers. They are prepared with phosphorus radicals such as  $-\text{CH}_2\text{PO(OH)}_2$ . The other type has phosphorus atoms linked to main carbon chains by oxygen atoms. The

preparation of  $\text{RC}-\overset{\text{O}}{\underset{\text{P}}{\text{O}}}-\text{CH=CH}_2$  is given.

Card 1/2

AUTHORS: Movsesyan, M. Yer, ~~Kabachnik, M. I.~~, Ioffe, S. T., Vatsuro, K. V. SOV/48-22-9-32/40

TITLE: Investigation of the Keto-Cis-Trans-Enol Equilibrium by Means of Infrared Absorption Spectra (Issledovaniye keto-tsia-trans-enol'nogo ravnovesiya pri pomoshchi spektrov infrakrasnogo pogloshcheniya)

PERIODICAL: Izvestiya Akademii nauk SSSR, Seriya fizicheskaya, 1958, Vol 22, Nr 9, pp 1126 - 1130 (USSR)

ABSTRACT: This paper is an attempt to show the cis-trans enol tautomerism in keto-enol compounds by means of infrared absorption and to estimate the relative numbers of stereoisomeric variants. The investigation covered the infrared absorption spectra of acetic ester, of ethyl ester, of cyclohexanonic- and of cyclopentanone carboxylic acids, of  $\alpha$  secondary butyl acetic ester, and of formyl phenyl acetic ester. Chloroform, benzene, toluene, diethyl ether, carbon tetrachloride and n-hexane served as solvents. The relative intensities of the absorption bands of the keto- and enol variants of the substances in question were compared with the equilibrium constants

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Investigation of the Keto-Cis-Trans-Enol Equilibrium  
by Means of Infrared Absorption Spectra

SOV/48-22-9-32/4o

of acetic ester found by chemical methods. Experimental chemical investigations of a number of keto-enol compounds showed (Ref 1) that the cis-fixed anols accurately adhere to Meyer's law. The equilibrium constant of substances which only exhibit a trans-enol form(trans-fixed enol) is independent of the solvent. Two series of experiments showed that 1) the choice of acetic ester as a standard solvent is justified and 2) that  $L'$  is a constant quantity. Hence it was possible to set up the formula (Ref 7)  $K_T = EL + E_1$ . Keto-enols, in the solution of which cis- and trans-enol variants are contained are also characterized by a linear function of  $K_T$  versus  $L$ . Quantitative measurements of the keto-enol equilibrium which were carried out by chemical methods and by infrared absorption spectra exhibit good accordance. Spectroscopic evidence also validates the general formula for the equilibrium constant of the keto-cis-trans-enol tautomerism. There are 6 figures and 7 references, 3 of which are Soviet.

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Investigation of the Keto-Cis-Trans-Enol Equilibrium  
by Means of Infrared Absorption Spectra

SOV/48-22-9-32/40

ASSOCIATION: Fizicheskiy institut im. P.N.Lebedeva Akademii nauk SSSR  
(Institute of Physics imeni P.N.Lebedev, AS USSR) Komissiya  
po spektroskopii Akademii nauk SSSR (Committee of Spectro-  
scopy, AS USSR) IEOS Akademii nauk SSSR (IEOS, AS USSR)

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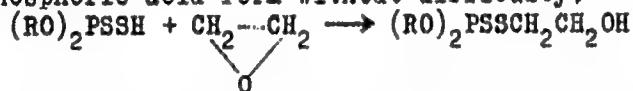
SOV/79-28-6-29/63

AUTHORS: Mastryukova, T. A., Odnoralova, V. N., Kabachnik, M. I.

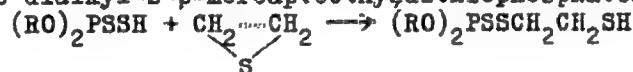
TITLE: On the Reaction of Dialkyldithiophosphates With Ethylene Sulfide (O reaktsii dialkil-ditiofosfatev s etilensul'fidom)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1563-1568 (USSR)

ABSTRACT: Some time ago the authors published a paper on the binding between dialkyldithiophosphates and ethylene oxide (Ref 1) on which occasion the  $\beta$ -oxysubstituted esters of dithiophosphoric acid form without difficulty:



In the present paper in this reaction ethylene sulfide was taken instead of the oxide. The investigation showed that the dialkyldithiophosphates combine with ethylene sulfide to dialkyl-S- $\beta$ -mercaptopethyl dithiophosphates:



Card 1/3

On the Reaction of Dialkyldithiophosphates With Ethylene Sulfide Sov/79-28-6-29/63

Contrary to the oxide reaction this binding demands more stringent conditions. The reduction with ethylene oxide takes place already at room temperature and that of ethylene sulfide only on heating. In Table 1 the constants and analyses of the obtained dialkyl S- $\beta$ -mercaptopethyldithiophosphates are shown. They are colorless and thermally unstable liquids, they are soluble in organic liquids, cannot be solved in water, and decompose in alkali liquors. The acetylation of their sulfohydryl groups takes place easily: with acetic anhydride in the presence of pyridine the corresponding acetyl derivatives were, for instance, obtained (see scheme 3); their constants and analyses are also mentioned (Table 1). The S- $\beta$ -mercaptopethyldithiophosphates react with diazomethane in the presence of methyl alcohol with the sulfohydryl group being methylated (scheme 4). Products of similar kind had been known already earlier (Ref 10); they belong to the effective insecticides arranged in systems. There are 2 tables and 8 references; 7 of which are Soviet.

Card 2/3

SOV / 79-28-6-29/63

On the Reaction of Dialkyldithiophosphates With Ethylene Sulfide

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds, AS USSR)  
Vsesoyuznyy nauchno-issledovatel'skiy institut iskusstvennogo volokna (All-Union Scientific Research Institute for Synthetic Fibers)

SUBMITTED: May 12, 1957

1. Ethylenes--Chemical reactions    2. Thiophosphates--Chemical reactions

Card 3/3

AUTHORS: Kabachnik, M. I., Godovikov, N. N., SOV/79-28-6-30/63  
Paykin, D. M., Shabanova, M. P., Gamper,  
N. M., Yefimova, L. F.

TITLE: Insecticides of Organophosphorus Compounds - Some  
Derivatives of Methylthiophosphinic- and Methyldithiophosphinic  
Acids (Fosfororganicheskiye insektitsidy,  
nekotoryye proizvodnyye metiltiofosfinovoy i  
metilditiofosfinovoy kislot)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp.  
1568 - 1573 (USSR)

ABSTRACT: The majority of phosphorus organic insecticides are  
derivatives of thiophosphoric-, dithiophosphoric- and  
pyrophosphoric acids (Refs 1 - 3). In publications also a  
few insecticides are described which are derivatives of  
phosphinic- and dithiophosphinic acids; among them are the  
methylphosphinates and methylthiophosphinates. The latter  
contain substituted aryl groups (Ref 4), the ethylxanthoyl-  
group, as well as other groups (Refs 4,5) and the  
O-ethyl-O-p-nitrophenylester of phenylthiophosphinic acid  
("E.P.N.") (Ref 6). This ester is the only insecticide

Card 1/3

Insecticides of Organophosphorus Compounds - Some  
Derivatives of Methylthiophosphinic - and  
Methyldithiophosphinic Acids

30V/79-28-6-30/63

of the series of thiophosphinic acids which is of practical importance. Therefore it was of interest to the authors to synthesize derivatives of alkylthio- and alkylmethyldithiophosphinic acids which have outer groupings analogous to those of well-known insecticides of thiophosphoric- and dithiophosphoric acid. The authors obtained from the dichloroanhydride of methylthiophosphinic acids the chloroanhydrides of the acid esters of methylthiophosphinic acid with methoxy-, ethoxy- and propoxygroups. Derivatives of methylthiophosphinic- and methyldithiophosphinic acid with groupings corresponding to well-known insecticides (Tiofos, Metafos, Karbofos, Potazan and Sistoks) were synthesized. The insecticide properties of the synthesized compounds were investigated in the laboratory using the autumn bugs on the plant "Eurygaster intergriceps Putt" as well as the fullgrown caterpillars on the plant "Psudococcus maritimus Ehrh". The insecticide effect of the mentioned synthesized compounds did not correspond to the activity of the known insecticides

Card 2/3

Insecticides of Organophosphorus Compounds - Some  
Derivatives of Methylthiophosphinic- and  
Methyldithiophosphinic Acids

SOV/79-28-6-50/65

of thiophosphoric- and dithiophosphoric acids. Only the preparation Gd-18 (a metaphos. analog) exceeds the effect of Metafos (Metafos) in its application against the bug of the first mentioned plant. There are 3 tables and 8 references, 3 of which are Soviet.

SUBMITTED: April 29, 1957

1. Insecticides--Synthesis 2. Phosphorous compounds (organic)  
--Synthesis

Card 5/3

NESMEYANOV, Aleksandr Nikolayevich, akademik; REUTOV, O.A., otv.red.toma;  
TOPCHIYEV, A.V., akademik, red.; KHUNYANTS, I.L., akademik, red.;  
KARACHNIK, M.I., akademik, red.; FREYDLINA, R.Kh., red.; KAN, E.I.,  
red.; LOSKUTOVA, I.P., red.izd-va; POLYAKOVA, T.V., tekhn.red.

[Selected works in four volumes] Izbrannye trudy v chetyrekh tomakh.  
Moskva, Izd-vo Akad.nauk SSSR. Vol.1. 1959. 712 p. (MIRA 12:12)

1. Chleny-korrespondenty AN SSSR (for Reutov, Freydlina).  
(Chemistry)

NESEMEYANOV, Aleksandr Nikolayevich, akademik; KABACHNIK, N.I., akademik,  
red.toma; TOPCHIYEV, A.V., akademik, red.; LOSKUTOVA, I.P.,  
red.izd-va; PRUSAKOVA, T.A., tekhn.red.

[Selected works in four volumes] Izbrannye trudy v chetyrekh  
tomakh. Moskva, Izd-vo Akad.nauk SSSR. Vol.3. 1959. 748 p.  
(MIRA 12:12)  
(Chemistry)

24(7)

SOV/51-6-5-5/34

AUTHORS: Mayants, L.S., Popov, Ye.M. and Kabanashik, M.I.

TITLE: Calculation of Characteristic Vibrations in Compounds of Phosphorus  
(Raschet kharakteristicheskikh kolistaniy soedineniy fosfora).  
Characteristic Vibrations of the Molecules  $\text{POCl}_3$ ,  $\text{POBr}_3$ ,  $\text{PCl}_3$  and  $\text{PBr}_3$   
(Kharakteristicheskiye kolibaniya molekul  $\text{POCl}_3$ ,  $\text{POBr}_3$ ,  $\text{PCl}_3$  and  $\text{PBr}_3$ )

PERIODICAL: Optika i Spektroskopiya, 1959, V-1 s, Nr 5, pp 589-593 (USSR)

ABSTRACT: The paper reports the results of calculation of vibrations of simple molecules with P-O and P-Cl bonds:  $\text{POCl}_3$ ,  $\text{POBr}_3$ ,  $\text{PCl}_3$  and  $\text{PBr}_3$ . Following Allen and Sutton (Ref 3) it is assumed that the equilibrium configurations of all these molecules belong to the  $\text{C}_{3v}$  group (see figure on p 593) and that their general formula can be written  $ZPY_3$ , where, Z = O or S and Y = Cl or Br. It follows that six fundamental frequencies should be observed in the vibrational spectra of the  $ZPY_3$  molecules: three of these frequencies should be fully symmetric and three doubly degenerate. The authors used in their calculations the published interpretations of the Raman spectra (Refs 3-5) and the following generalised coordinates: fluctuations of the bond lengths P-Z and P-Y<sub>i</sub> (i = 1, 2, 3) and of the angles Y<sub>i</sub>...P...Y<sub>j</sub> (i, j = 1, 2, 3) and Z...P...Y<sub>i</sub> (i = 1, 2, 3). These coordinates were denoted by letters

Card 1/2

SCJ/51-6-5-3/24  
Calculation of Characteristic Vibrations in Compounds of Phosphorus. Characteristic  
Vibrations of the Molecules  $\text{PCl}_3$ ,  $\text{POBr}_3$ ,  $\text{PSCl}_3$  and  $\text{PSBr}_3$ .

$Q$ ,  $q_i$ ,  $\gamma_k$  ( $k \neq i, j$ ) and  $\delta_i$  respectively. The equilibrium bond lengths were taken to be  $\text{P=O} = 1.58 \text{ \AA}$ ,  $\text{P=Cl} = 2.02 \text{ \AA}$ ,  $\text{P=S} = 1.94 \text{ \AA}$ ,  $\text{P=Br} = 2.18 \text{ \AA}$ . Angles  $\gamma_i$  and  $\gamma_j$  were assumed to be tetrahedral. The force constants were chosen to obtain the best possible agreement between the calculated and observed Raman and infrared absorption frequencies. Designations of the force constants are in Table 1 and their values (in  $10^6 \text{ cm}^{-2}$ ) in Table 2. The calculations yielded frequencies and forms of the normal vibrations of the four molecules and the sensitivities of these frequencies to changes in the force constants, atomic masses, bond lengths and angles. The results are given in Tables 3-5. The form of fully symmetric vibrations  $\nu_1$  ( $\text{P=O}$  frequencies in  $\text{POCl}_3$  and  $\text{POBr}_3$  and  $\text{P=S}$  frequencies in  $\text{PSCl}_3$  and  $\text{PSBr}_3$ ) should, strictly, be determined by the coordinate  $Q$  but Table 3 shows that it is affected also by the coordinates  $q$ ,  $\gamma$  and  $\delta$ . There are 1 figure, 5 tables and 10 references, 5 of which are Soviet, 2 English, 2 German and 1 French.

SUBMITTED: June 11, 1959  
Card 2/2

AUTHORS: Mayants, L.S., Popov, Ye.M. and Kabachnik, M.I. SOV/51-7-2-5/34

TITLE: Calculation of the Characteristic Vibrations of Phosphorus Compounds (Rechet kharakteristichnykh kolebaniy soyedineniy fosfura). I. Characteristic Vibrations of the  $(CH_3O)_3PO$  and  $(CH_3O)_3PS$  Molecules (II. Kharakteristichnye kolebaniya molekul  $(CH_3O)_3PO$  i  $(CH_3O)_3PS$ ).

PERIODICAL: Optika i spektroskopiya, 1959, Vol 7, Nr 2, pp 170-177 (USSR)

ABSTRACT: In Part I (Ref 1) the authors reported the results of calculation of the normal vibrations of the  $POCl_3$ ,  $POBr_3$ ,  $PSCl_3$  and  $PSBr_3$  molecules and discussed vibrations of these molecules corresponding to the  $P = 0$  and  $P = S$  frequencies. It was shown that the symmetrical vibration  $\nu_1$  of the four molecules mentioned above has not quite the form characteristic of the  $Q$  coordinate, which refers to the change of the  $P = 0$  or  $P = S$  bond length. In order to determine the effect of coordinates which are further from  $Q$  on the vibration  $\nu_1$ , the authors calculated the fully symmetric vibrations of the  $(CH_3O)_3PO$  and  $(CH_3O)_3PS$  molecules for certain estimated values of the force constants and they determined the sensitivity of frequencies to changes of these constants. Of the possible rotational isomers of the  $(CH_3O)_3PO$  and  $(CH_3O)_3PS$  molecules four models were selected (figure on p 171). The models I and II have

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Calculation of the Characteristic Vibrations of Phosphorus Compounds. II. Characteristic Vibrations of the  $(CH_3O)_3PO$  and  $(CH_3O)_3PS$  Molecules

SOV/51-7-2-5/34

the symmetry  $C_{3V}$ , the model III has  $C_3$  symmetry (the C--O bonds lie in the plane normal to the third-order axis) and the model IV has  $C_S$  symmetry. The results obtained (Tables 2-6) and those of Part I (Ref 1) lead to the conclusion that the vibration  $\nu_1$  is very characteristic in form and frequency of the coordinate Q and related coordinates. The  $P = 0$  and  $P--O$  frequencies are used to show that the models I and III are most likely isomers in solutions of  $(CH_3O)_3PO$ . There are 1 figure, 6 tables and 20 references, 11 of which are Soviet, 5 English, 3 German and 1 from an international journal.

SUBMITTED: November 24, 1958

Card 2/2

5.3630

77059  
SOV/62-59-12-13/43

AUTHORS:

Kabachnik, M. I., Gilyarov, V. A., Tsvetkov, Ye. N.

TITLE:

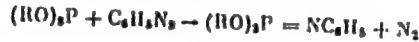
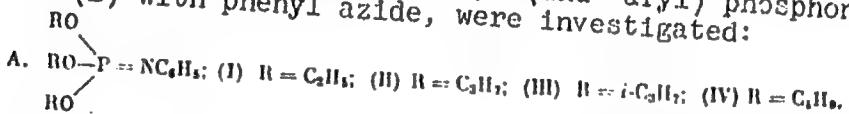
Concerning Imides of Phosphorus Acids. Infrared Absorption Spectra of Imidophosphates and Imidophosphonates

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 12, pp 2135-2141 (USSR)

ABSTRACT:

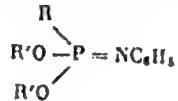
The IR absorption spectra of trialkyl N-phenylimidophosphates (A) which were obtained previously by reaction of trialkylphosphites (M. I. Kabachnik, V. A. Gilyarov, Izv. AN SSSR. Otd. khim. n. 1956, 790) and dialkyl N-phenylimidoalkyl-(and -aryl) phosphonates (B) with phenyl azide, were investigated:



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Concerning Imides of Phosphorus Acids.  
 Infrared Absorption Spectra of Imido-  
 phosphates and Imidophosphonates

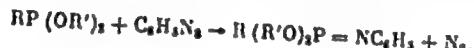
77059  
 SOV/62-59-12-13/43



(V)  $\text{R}=\text{CH}_3$ ;  $\text{R}'=i\text{-C}_3\text{H}_7$   
 (VI)  $\text{R}=\text{CH}_3$ ;  $\text{R}'=\text{C}_6\text{H}_5$   
 (VII)  $\text{R}=\text{C}_6\text{H}_5$ ;  $\text{R}'=\text{C}_3\text{H}_7$

(VIII)  $\text{R}=\text{C}_6\text{H}_5$ ;  $\text{R}'=\text{C}_6\text{H}_5$ ; (IX)  $\text{R}=\text{C}_6\text{H}_5$ ;  $\text{R}'=\text{C}_6\text{H}_5$ ; (X)  $\text{R}=\text{C}_6\text{H}_5$ ;  $\text{R}'=\text{C}_6\text{H}_5$   
 (XI)  $\text{R}=\text{C}_6\text{H}_5$ ;  $\text{R}'=\text{C}_6\text{H}_5$ ; (XII)  $\text{R}=\text{C}_6\text{H}_5$ ;  $\text{R}'=\text{C}_6\text{H}_5$ ,

Most of the above compounds were synthesized for the present investigation by the reaction between dialkyl alkyl-(and aryl)-phosphonates and phenyl azide:



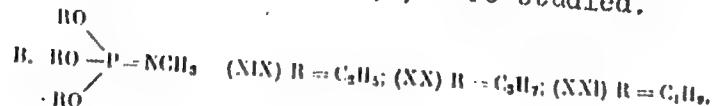
Card 2/12

IR spectra of the above compounds have a strong absorption band at  $1350-1385 \text{ cm}^{-1}$ , which indicates the presence of the  $\text{P}=\text{N}$ -group. The IR spectra of

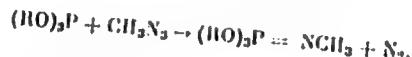
Concerning Imides of Phosphorus Acids.  
Infrared Absorption Spectra of Imido-  
phosphates and Imidophosphonates

77059  
SOV/62-59-12-13/43

triethyl N-acetylimidophosphate (XIII) and trialkyl  
N-methylimidophosphates (C) were studied.



The above compounds were obtained by reaction of  
methyl azide with trialkyl phosphites.



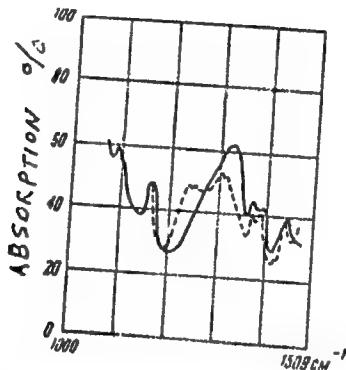
In the IR spectrum of compound XIII, a strong absorption  
band at  $1350$  and  $1385 \text{ cm}^{-1}$  was observed. Compound  
XIX also shows strong absorption at  $1325 \text{ cm}^{-1}$ . On  
exposure to air, its intensity decreases and the

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Concerning Imides of Phosphorus Acids.  
Infrared Absorption Spectra of Imido-  
phosphates and Imidophosphonates

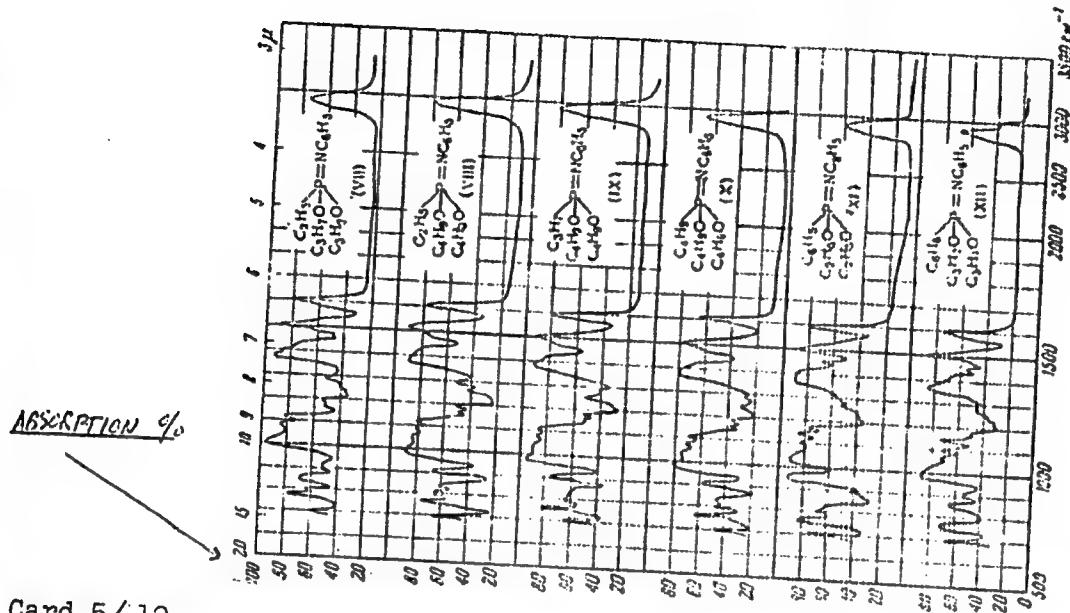
77069  
SOV/62-59-12-13/43

intensity of the band at  $1250 \text{ cm}^{-1}$  characteristic of  
 $\text{P} = \text{O}$  bond increases, thus indicating that the above  
compound is easily hydrolyzed.

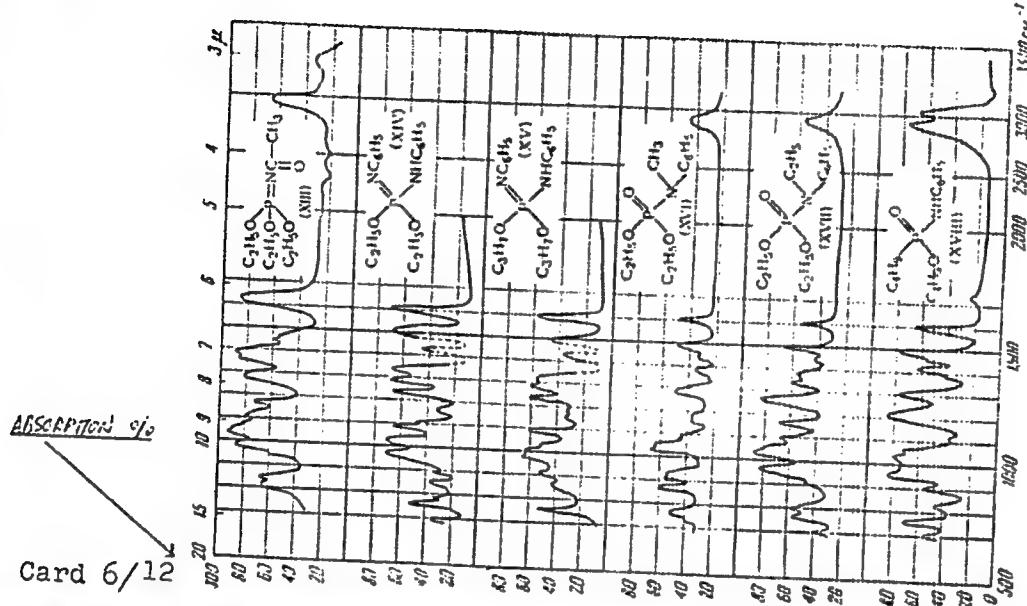


Card 4/12

77069, 30V/62-59-12-13/43

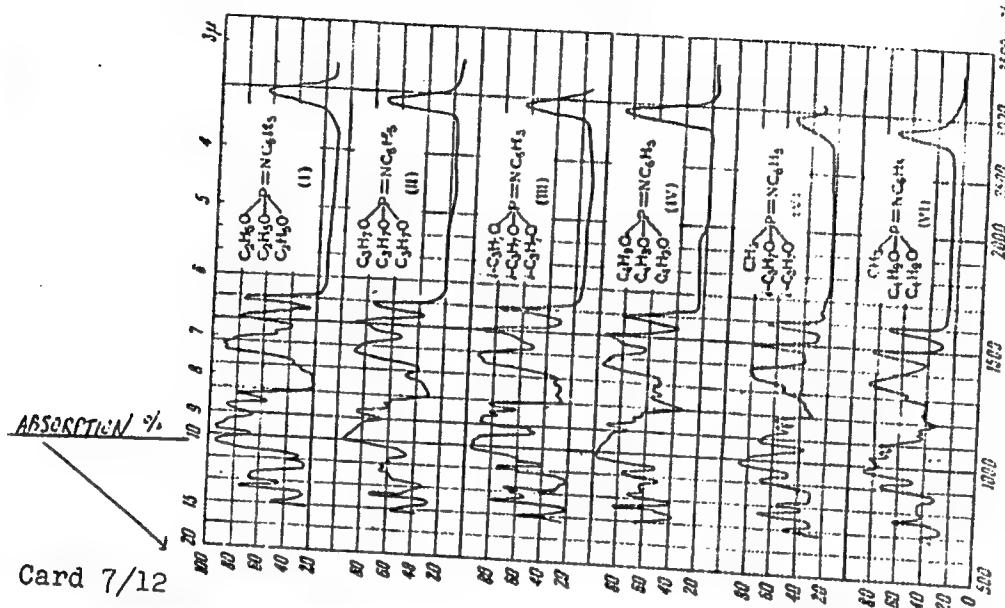


77069, SOV/62-59-12-13/43



# Concerning Imides of Phosphorus Acids Infrared Absorption Spectra of Imido- phosphates and Imidophosphonates

77069  
SOV/62-59-12-13/43



77069  
SOV/62-59-12-13/43

IR spectra were taken on a double beam Dianov-Klokov spectrometer based on a IK-Spectrometer VIKS-M2-N 11. The yields of obtained products are given below:

FORMULA	YIELD (%)	bp (PRESSURE IN mm)	$n^{20}_D$	$d^{20}_T$
$\text{C}_4\text{H}_9\text{O} \text{P} \begin{cases} \text{NC}_2\text{H}_5 \\ \text{CH}_3 \end{cases}$	66,7	107,5-108 (0,5)	1,5050	1,0066
$\text{C}_4\text{H}_9\text{O} \text{P} \begin{cases} \text{NC}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{cases}$	53,0	102 (1)	1,5088	1,0185
$\text{C}_4\text{H}_9\text{O} \text{P} \begin{cases} \text{NC}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{cases}$	66,3	117-118 (1)	1,5045	0,9965

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Concerning Imides of Phosphorus Acids.  
 Infrared Absorption Spectra of Imido-  
 phosphates and Imidophosphonates

77069  
 SOV/62-59-12-13/43

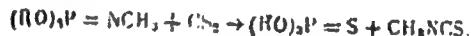
FORMULA	YIELD (%)	b.p. (PRESSURE 11 mm)	$n_D^{20}$	$\nu_1^{20}$
$\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{P} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NC}_6\text{H}_5$ $\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_5$	61,5	123-124 (1)	1,5010	0,9807
$\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{P} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NC}_6\text{H}_5$ $\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_5$	71,5	131-132 (1,5)	1,4990	0,9509
$\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{P} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NC}_6\text{H}_5$ $\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_5$ CYCLO	85,0	148 (0,5)	1,5000	1,0150
$\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{P} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NC}_6\text{H}_5$ $\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_5$	54	125 (1)	1,5708	1,1033
$\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{P} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NC}_6\text{H}_5$ $\text{C}_6\text{H}_5\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_5$	72,0	127-129 (1)	1,5573	1,0770

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Concerning Imides of Phosphorus Acids.  
Infrared Absorption Spectra of Imido-  
phosphates and Imidophosphonates

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SOV/62-59-12-13/43

Trialkyl N-methylimidophosphates are colorless liquids,  
easily hydrolyzed by water with formation of methylimi-  
des of dialkylphosphoric acids. They react with  
 $\text{CS}_2$  as follows:



E. M. Popov, I. F. Lutchenko, V. N. Smorchikov, I. Ya. Kachkurova, I. V. Obreimov took part in this work. There are 4 figures; 2 tables; 12 references, 1 German, 2 U.S., 2 U.K., 7 Soviet. The 4 U.S. and U.K. references are: L. W. Daasch, J. Amer. Chem. Soc. 76, 3403, (1954); L. W. Daasch, D. C. Smith, Analyt. Chem. 23, 853 (1951); D. E. Corbridge, J. Appl. Chem. 6, 10, 456 (1956); D. E. Corbridge, E. J. Lowe, J. Chem. Soc. 1954, 4555.

Card 11/12

5.3630

77070  
SOV/62-59-12-14/43

AUTHORS:

Kabachnik, M. I., Medved', T. Ya.

TITLE:

Vinylphosphonic Acid and Some of Its Derivatives

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 12, pp 2142-2145 (USSR)

ABSTRACT:

Vinylphosphonyl dichloride can be obtained by dehydrochlorination of  $\beta$ -chloroethylphosphonyl dichloride over barium chloride in a quartz tube, at 330-340°; yield, 85.6%; bp 67-69° (21 mm);  $n_D^{20}$  1.4808. The structure of the acid dichloride was confirmed by conversion to the known diethyl vinylphosphonate. The methyl and the isopropyl esters were also prepared, as well as the phenyl ester, prepared by treatment of the acid dichloride with phenol and triethylamine; yield, 84%; bp 109.5-110°.

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## Vinylphosphonic Acid and Some of Its Derivatives

77070

SOV/62-59-12-14/43

( $1 \times 10^{-4}$  mm);  $n_D^{20}$  1.5571. The acid dichloride and trimethylene glycol, in the presence of triethylamine, form the cyclic trimethylene ester, in 53% yield; bp

129-130° (2 mm);  $n_D^{20}$  1.4775. Diethyl vinylphosphonate

adds bromine to form diethyl  $\alpha, \beta$ -dibromoethylphosphonate: the reaction is accompanied by dehydrobromination forming diethyl  $\alpha$ -bromovinylphosphonate. Treatment of vinylphosphonyl dichloride with 4 moles of dimethylamine formed the tetramethyldiamide of vinylphosphonic acid in

52% yield; bp 82° (3mm);  $n_D^{20}$  1.4732. Hydrolysis of the acid dichloride formed vinylphosphonic acid,  $n_D^{20}$  1.4737.

On distillation under reduced pressure, the acid apparently forms pyrovinyphosphonic acid, a colorless, syrupy liquid,  $n_D^{20}$  1.4851. The e are 8 references, 5 Soviet, 1 French,

Card 2/3

5(3)

SOV/79-29-5-9/75

AUTHORS:

Mastryukova, T. A., Shipov, A. E., Kabachnik, M. I.

TITLE:

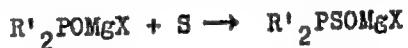
Method of Preparation of Dialkyl-Thiophosphinic Acids (Metod polucheniya dialkiltiofosfinovykh kislot)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 5,  
pp 1450 - 1453 (USSR)

ABSTRACT:

This paper reports on a method of synthesizing dialkyl-thiophosphinic acids with different radicals on the phosphorus. The scheme of this method can be represented by the following equations:



Card 1/2

According to this new method  $R_2PSOH$ -acids ( $R = C_2H_5$ ,  $C_3H_7$ , iso- $C_3H_7$ ,  $C_4H_9$ , iso- $C_4H_9$  and  $C_6H_5CH_2$ ) were obtained. The yields were 64 - 88%. In the table constants, neutralization equivalents,

Method of Preparation of Dialkyl-Thiophosphinic Acids SOV/79-29-5-9/75

data of the elementary analysis and yields of the resulting acids are summarized. The formation of the dialkyl-thiophosphinic acids according to the new scheme was confirmed by the synthesis of the ammonium salt of the dipropyl-thiophosphinic acid. There are 1 table and 16 references, 10 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR  
(Institute of Elemental-Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: March 27, 1958

Card 2/2

5(3)

## AUTHORS:

Kabachnik, M. I., Golubeva, Ye. I., Sov/79-29-5-57/75  
Paykin, D. N., Shabanova, M. P., Gamper, N. M., Yefimova, L. P.

## TITLE:

Organophosphorus Insecticides (Fosfororganicheskiye  
insektitsidy).  $\beta$ -Fluoroethyl Ester of the Acids of  
Phosphorus (  $\beta$ -Ftoretilovyye estiry kislot fosfora)

## PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1671-1680 (USSR)

## ABSTRACT:

The following compounds were prepared:  $\beta$ -fluoro-triethyl-phosphite (Ye-11),  $\beta$ - $\beta'$ -difluoro-triethyl-phosphite (Ye-20),  $\beta$ , $\beta'$ -difluoro-diethyl-phosphite (Ye-17),  $\beta$ -fluoro-triethyl-phosphate (Ye-32),  $\beta$ -fluoro-triethyl-thione-phosphate (Ye-3),  $\beta$ , $\beta'$ -difluoro-triethyl-thione-phosphate (Ye-12),  $\beta$ , $\beta'$ -fluoro-diethyl-thione-phosphate (Ye-30), 0,S-diethyl-0- $\beta$ -fluoroethyl-thiophosphate (Ye-18), 0,0-diethyl-S- $\beta$ -fluoroethyl-thiolphosphate (Ye-31), 0,0-diethyl-S- $\beta$ -fluoroethyl-dithiophosphate (Ye-33),  $\beta$ -fluoro-ethyl dichloro-thione-phosphate (Ye-49),  $\beta$ -fluoro-diethyl-chloro-thione-phosphate (Ye-48),  $\beta$ -fluoro-diethyl-4-nitrophenyl-thione-phosphate (Ye-50), 0,0- $\beta$ -fluoro-diethyl- $\alpha$ , $\beta$ -dicarbethoxy-ethyl-dithiophosphate (Ye-51),  $\beta$ -fluoro- $\beta'$ -ethyl-mercapto-triethyl-thione-phosphate (Ye-52),  $\beta$ -fluoro-diethyl-ethyl-phosphinate

Card 1/2

2

Organophosphorus Insecticides.  $\beta$ -Fluoroethyl Ester of the SOV/79-29-5-57/75  
Acids of Phosphorus

(Ye-9),  $\beta$ -fluoro-diethyl-methyl-phosphinate (Ye-19),  $\beta,\beta'$ -difluoro-diethyl-methyl-phosphinate (Ye-28),  $\beta-\beta'$ -difluoro-diethylmethyl-thione-phosphinate (Ye-29),  $\beta$ -fluoroethyl-methyl-chloro-thione-phosphinate (Ye-13),  $\beta$ -fluoro- $\beta'$ -ethyl-mercaptop-diethyl-methyl-thione-phosphinate (Ye-25),  $\beta$ -fluoroethyl-n-nitro-phenyl-methyl-thione-phosphinate (Ye-27), O- $\beta$ -fluoroethyl-S- $\alpha,\beta$ -dicarbalkoxy-ethyl-methyl-dithiophosphinates (Ye-14, Ye-15, Ye-16), monomethyl-methyl-thione-phosphinate (Ye-37), O-ethyl-S- $\beta$ -fluoro-ethyl-methyl-thiolphosphinate (Ye-38), O-methyl-S- $\beta$ -fluoro-ethyl-methyl-thiophosphinate (Ye-39), O- $\beta$ -fluoro-diethyl-methyl-monothiophosphinate (Ye-10), O-ethyl-S- $\beta$ -fluoroethyl-methyl-dithiophosphinate (Ye-35), O-methyl-S- $\beta$ -fluoro-ethyl-methyl-dithiophosphinate (Ye-36). Boiling point, refraction of light, density and chemical composition as well as the course of synthesis and the yield are given. The toxic properties were tested on *pseudococcus maritimus* Ehr. and on *Calliptamus italicus* L. (Table). Only the preparations Ye-31 and Ye-36 showed insecticidal effect which is equal to that of Thiophos and Mercaptophos. There are 1 table and 15 references, 11 of

Card 2/3

2

5 (3)

AUTHORS:

Kabachnik, M. I., Golubeva, Ye. I., S07/79-29-5-33/15  
Paykin, D. M., Shebanova, N. P., Gamper, N. N., Yefimova, L. P.

TITLE:

Organophosphorus Insecticides (Fosfororganicheskiye  
insektitsidy). Some Esteramides of the Acids of Phosphorus  
Containing  $\beta$ -Fluoro-ethyl Groups (Nekotoryye estiroamidy kislot  
fosfora, soderzhashchiye  $\beta$ -ftoratil'nyye gruppy)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 5,  
pp 1680-1683 (USSR)

ABSTRACT:

The compounds formed correspond to the formula type

$$\begin{array}{c} \text{RO} \\ | \\ \text{FCH}_2\text{CH}_2\text{O} \end{array} \begin{array}{c} \text{P} \\ || \\ \text{O(S)} \\ | \\ \text{N}(\text{CH}_3)_2 \end{array}$$

The following compounds were produced: methyl- $\beta$ -fluoro-ethyl-chloro-phosphate (Ye-40), the corresponding ethyl-(Ye-41), isopropyl-(Ye-43), and isobutyl-(Ye-46) compounds. Di- $\beta$ -fluoro-diethyl-chloro-phosphate (Ye-21), methyl- $\beta$ -fluoro-ethyl-dimethyl-amidophosphate (Ye-44), the corresponding ethyl-(Ye-42), isopropyl-(Ye-45), and isobutyl-(Ye-47) compounds.  $\beta$ -fluoro-diethyl-dimethylamido-thioneophosphate (Ye-53).

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Organophosphorus Insecticides. Some Esteramides of  
the Acids of Phosphorus Containing  $\beta$ -Fluoro-ethyl Groups

SOV/79-29-5-59/75

The preparation is described; boiling temperature, refraction, density, and composition are presented in tables (Tables 1 and 2). The toxic properties were tested with *Pseudococcus maritimus* Ehr. and *Calliptamus italicus* L. The compounds produced have only a weak insecticidal effect. There are 3 tables and 2 Soviet references.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds of the Academy of Sciences USSR)

SUBMITTED: February 6, 1958

Card 2/2

5 (3)

## AUTHORS:

Popov, Ye. M., Mastryukova, T. A.,  
Rodionova, N. P., Kabachnik, M. I. 307/79-29-6-50/72

## TITLE:

The Vibration Spectra of the Organophosphorus Compounds  
(Kolebatel'nyye spektry fosfororganicheskikh soyedineniy).  
On the Problem of the Characteristics of the Frequency P=S  
(K voprosu o kharakteristichnosti chastoty P=S)

## PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 6,  
pp 1998-2006 (USSR)

## ABSTRACT:

The investigation of the vibration spectra of phosphorus- and organophosphorus compounds leads to the conclusion that in molecules with the group P=O a vibration occurs in which this group plays the main role. For the structure and the analysis of the phosphorus compounds also the spectral characteristics of the group P=S is of interest. In order to determine the so-called characteristic frequencies of the group P=S the infrared spectra and the Raman effects of the organothiophosphorus compounds were obtained in parallel to the corresponding thiophosphorus and phosphorus compounds. In the compounds investigated the bands connected with the group

Card 1/3

The Vibration Spectra of the Organophosphorus Compounds. On the Problem of the Characteristics of the Frequency P=S SOV/79-29-6-50/72

P=S are in the range from 750 to 580  $\text{cm}^{-1}$ . The frequency of the normal vibration of the molecule in which this group participates, is considerably subjected to the structural influences; in this connection each type of the substituents changes the frequency by a certain amount. The frequencies which are related to group P=S (Table 2) conserve their constant values only if the central phosphorus atom is surrounded by the same atoms or radicals. The bonds and the angles which have no common atom with the group P=S do not participate in the given oscillation and practically do not influence the frequency. A final explanation could not yet be given. The authors thank L. S. Mayants for valuable advice. There are 2 figures, 2 tables, and 18 references, 4 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR  
(Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

Card 2/0

2

5 (3)

## AUTHORS:

Mastryukova, T. A., Melent'yeva, T. A., SOV/79-29-7-18/83  
Shipov, A. E., Kabachnik, M. I.

## TITLE:

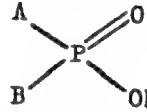
The Application of the Hammette (Gammette ?) Equation to the  
Ionization Constants of Organophosphoric Acids in 7- and 80 %  
Alcohol (Primeneniye uravneniya Gammetta k konstantam ionizatsii  
fosfororganicheskikh kislot v 7 i 80 % spirte)

## PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2178-2182 (USSR)

## ABSTRACT:

In connection with investigations in the field of the tautomerism  
of organophosphorus compounds (Ref 3) the authors determined the  
apparent ionization constants of the phosphoric acid series of  
the general formula:



in 7- and 80 % alcohol. It  
was of interest to investigate to what extent the Hammette  
(Gammette ?) equation ( $\lg \frac{K}{K_0} = \rho \sum \sigma$ ) holds in the case of these  
solvents. It was especially interesting because the authors  
determined the ionization constants of some types of phosphoric  
acids which earlier had not been measured, i.e. of diaryl

Card 1/2

The Application of the Hammette (Gammette ?) Equation to the Ionization Constants of Organophosphoric Acids in 7- and 80 % Alcohol

SOV/79-29-7-18/83

phosphinic-(A=B=Ar) and diaryl phosphoric acid (A=B=ArO). The results obtained, together with some other data marked with asterisks (Ref 3) are given in table 1. The constants  $\sigma$  for the aroxy groups at the phosphorus have hitherto been unknown. Their apparent ionization constants ( $pK_1$  and  $pK_2$ ) of phenyl and diphenyl phosphoric acid as well as of tolyl and ditolyl phosphoric acid were determined in 50 % alcohol as far as the constants  $\sigma$  and  $pK$  for the ionization of phosphoric acids in this solvent are computed precisely enough (Ref 1). The results obtained (Table 2), from which the mean values  $\sigma$  for the groups  $C_6H_5O$  and  $C_7H_7O$  were computed, may be found in the last column of table 2. The values found  $\sigma$  were used for plotting the diagram  $pK_f(\sum\sigma)$  for 7- and 80 % alcohol and then exactly determined by means of the data obtained from the two solvents. The final mean values for the groups  $C_6H_5O$  and  $CH_3C_6H_4O$  are written down provisionally. There are 1 figure, 4 tables, and 17 references, 3 of which are Soviet.

Card 2/4

2

5 (3)

## AUTHORS:

Kabachnik, M. I., Godovikov, N. N., SOV/79-29-7-19/83  
 Paykin, D. M., Shabanova, M. P., Yefimova, L. F., Gamper, N. M.

## TITLE:

Organophosphorous Insecticides (Fosfororganicheskiye insektitsidy).  
 VI. Amidoesters of the Thio- and Dithiophosphoric Acids  
 Containing a  $\beta$ -Ethyl Mercapto Ethyl Grouping (VI. Amidoefiry  
 tiofosfornoy i ditiofosfornoy kislot, soderzhashchiye  $\beta$ -estil-  
 merkaptoetil'nyyu gruppovku)

## PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2182-2190 (USSR)

## ABSTRACT:

In 1936 G. Schrader (Ref 1) discovered the insecticide properties of the phosphoric- and thiophosphoric acid amides. The derivatives of the dialkyl amido- and dialkyl amidothiophosphoric acid of the type

$$\begin{array}{c}
 \text{R}_2\text{N} \quad \text{O}(\text{S}) \\
 \diagup \quad \diagdown \\
 \text{P} \\
 \diagdown \quad \diagup \\
 \text{R}'\text{O} \quad \text{Ac}
 \end{array}$$

denote alkyls and Ac substitutes of acyl character such as Cl, F, CN, CNO,  $\text{CH}_3\text{COO}$  and others, which he synthesized show contact insecticide properties of vegetative effect. Other compounds of similar type with the phenyl- (Refs 1, 2), azide (Ref 3), and other groups (Refs 4-7) followed. Most of the

Card 1/3

Organophosphorous Insecticides. VI. Amidoesters of  
the Thio- and Dithiophosphoric Acids Containing a  $\beta$ -Ethyl Mercapto Ethyl  
Grouping

SOV/79-29-7-19/83

insecticides of phosphoric acid have only a weak contact- and a strong vegetative effect. Some of them are used in practical applications (Ref 8). On the other hand, it was of interest to examine this activity in the amido esters of thiophosphoric and dithiophosphoric acid with a  $\beta$ -ethyl mercapto ethyl grouping since it could be assumed that they would also show a strong vegetative activity. These esters have hitherto remained unknown with few exceptions (Refs 11, 12). The compounds (I), (II), and (III), the first two of which were obtained as acid chlorides according to scheme 3, were used as initial products for these amido esters. In reacting the above acid chlorides with  $\beta$ -oxydiethyl sulphide in the presence of powder sodium hydroxide the thiophosphates (Gd-50), (Gd-52), and (Gd-64) (Scheme 4) resulted. The compounds obtained were isomerized into the thiophosphates (Gd-53), (Gd-54), and (Gd-66) at 160-170° during 8-10 hours (Scheme 5). Moreover, the thio-phosphates (Gd-55) and (Gd-56) were synthesized by the reaction according to scheme 6. The constants and yields of the new insecticides are listed in table 1 (details are given in the

Card 2/3

Organophosphorous Insecticides. VI. Amidoesters of the SOV/79-29-7-19/83  
Thio- and Dithiophosphoric Acids Containing a  $\beta$ -Ethyl Mercapto Ethyl Grouping

experimental part and in tables 2 and 3). In heating tetra-methyl diamidochlorophosphate with  $P_2S_5$  tetramethyl diamido-thiophosphate is formed by replacement of the oxygen atom by sulphur. Some amido esters such as (Gd-53), (Gd-54), and (Gd-56) show a vegetative activity against spinning-mites. There are 3 tables and 17 references, 11 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR  
(Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: June 20, 1958

Card 3/3

5(2,3,4)  
AUTHORS:

Kabachnik, M. I., Academician,  
Mastryukova, T. A., Shipov, A. E., Melent'yeva, T. A. SOV/20-124-5-27/62

TITLE:

The Use of Hammett's Equation in the Theory of Tautomeric Equilibrium (Primeneniye uravneniya Gammetta v teorii tautomernogo ravnovesiya). The Thion-Thiol Tautomerism of Thiophosphoric Compounds (Tion-tiol'naya tautomeriya tiofosfornykh soyedineniy)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 5, pp 1061-1064  
(USSR)

ABSTRACT:

The first and second authors have proved (together with S. T. Ioffe) that Broensted's (Brensted) equation is applicable to organo-thiophosphoric acids (Ref 3). The first author has also found that the relation between the equilibrium constant and the ionization constants of the forms  $K_{1S} = K_{1S}/K_{2S}$  is of fundamental importance in the theory of tautomeric equilibrium. In accordance therewith the theory of Broensted-Izmaylov regarding the acid-alkali protolytic equilibrium (Ref 2) has been applied to the tautomeric equilibrium in solutions. Thus, a quantitative interpretation of the ion theory

Card 1/4

The Use of Hammett's Equation in the Theory of  
Tautomeric Equilibrium. The Thion-Thiol Tautomerism of Thiophosphoric Compounds

SOV/20-124-5-27/62

of tautomerism has been suggested. The fact that Broensted's equation is applicable to the organo-thiophosphoric acids rendered determination of the position of the tautomeric equilibrium of dialkyldithio-phosphoric acids (Ref 3) and of the alkylthioalkyl-phosphinic acids (Ref 4) possible. There was every reason to use Hammett's equation for the purpose stated in the title. This was possible with the aid of two equations (1). It must be borne in mind, however, that the experimental measurements did not give the ionization constants of individual forms but certain effective constants  $K_a$ , which have a certain relation ((2), Ref 7) to the ionization constants of the forms. The substitution of  $K_1$  and  $K_2$  from equations (1a) and (1b) in relation (2) enables the constant  $K_a$  to be easily derived from the parameters of Hammett's equation (3). This relationship is graphically expressed with the coordinates  $pK$  and  $\sum \sigma$  by the curve  $pK_a = \varphi(\sum \sigma)$ , which is asymptotic to the two straight lines I and II (Fig 1).

Card 2/4

The Use of Hammett's Equation in the Theory of  
Tautomeric Equilibrium. The Thion-Thiol Tautomerism of Thiophosphoric  
Compounds

SOV/20-124-5-27/62

This facilitates a derivation of the experimental method of the quantitative solution to the problem. Table 1 gives the effective ionization constants ( $pK_a$ ) of the series of the tautomeric acids  $RR'P(S)OH \rightleftharpoons RR'P(O)SH$ , which differ by the R and R' groups and consequently by the  $\sum \sigma$  values (calculated according to references 6,9). As may be seen from figure 2, there is a good linear relationship for the points having  $\sum \sigma$  values between -3 and -2. From the results obtained the parameters of the straight lines  $pK_a = pK_1^0 - \rho_1 \sum \sigma$  were determined, which define the ionization constants of the thion forms in 7 % and 80 % alcohol (least squares method, reference 10). The values found for the constants of the tautomeric equilibrium must satisfy Hammett's equation:  $\log K_T = \log K_T^0 + \rho \sum \sigma$  (5). Figure 3 shows the diagrams illustrating the dependence of  $\log K_T$  on  $\sum \sigma$  based on the data of the table 1. As may be seen, the relationship according to Hammett has been expressed well

Card 3/4

The Use of Hammett's Equation in the Theory of SOV/20-124-5-27/62  
Tautomeric Equilibrium. The Thion-Thiol Tauromerism of Thiophosphoric  
Compounds

enough. Finally, the percentages of the thiol forms were calculated with the aid of the resulting equations for the solutions of all substances investigated (Table 1). Based on the deviations of the linear dependence of Hammett's  $pK_a$  of the tautomeric acids from  $\sigma$  (or  $\Sigma\sigma$ ), a quantitative analysis of tautomeric equilibrium can thus be given. There are 3 figures, 1 table, and 10 references, 7 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR  
(Institute for Elemental-Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: January 26, 1959

Card 4/4

5(2)  
AUTHORS:

Kabachnik, M. I. Academician,  
Tsvetkov, Ye. N., Chang Jung-jui

SOV/20-125-6-23/61

TITLE:

A Method of Synthesizing Acid Esters of Phosphinous  
Acids (Metod sinteza kislykh efirov fosfinistykh kislot)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 6,  
pp 1260-1262 (USSR)

ABSTRACT:

No practicable synthesis methods exist for alkyl dichlorophosphines which usually serve as initial substances for the production of various derivatives of the alkyl-phosphinous acids, among them their acid esters. These derivatives have therefore been scarcely investigated. The authors give a survey of publications on the synthesis mentioned in the title (Refs 1 - 11). The present paper describes the general synthesis method of the acid esters of the alkyl- and aryl-phosphinous acids by means of the hydrolysis of corresponding complete esters according to an earlier method (Refs 12). For this purpose it is not necessary that the complete esters are isolated in pure state. This process is caused by the action of water on the reaction mixture. The water is produced by the interaction

Card 1/2

GAFTER, Yevgeniy Leonidovich; KABACHNIK, M.I., akademik, otv.red.;  
KORSHAK, V.V., otv.red.; ZOSKUTOVA, T.P., red.izd-va;  
KUZ'MIN, I.V., tekhn.red.

[Organophosphorus monomers and polymers] Fosfororganicheskie  
monomery i polimery. Moskva, Izd-vo Akad.nauk SSSR, 1960.  
287 p.

(MIRA 13:3)

1. Chlen-korrespondent AN SSSR (for Korshak).  
(Phosphorus organic compounds)

SHATENSHTEYN, Aleksandr Isayevich; KABACHNIK, M.I., akademik, otd.red.;  
POVAROV, L.S., red.izd-va; POLENOVA, T.P., tekhn.red.

[Isotopic exchange and substitution of hydrogen in organic  
compounds from the standpoint of the theory of acids and bases]  
Isotopnyi obmen i zamenshenie vodoroda v organicheskikh soedi-  
neniakh v svete teorii kislot i osnovani. Moskva, Izd-vo Akad.  
nauk SSSR, 1960. 394 p. (MIRA 13:3)

(Isotopes) (Hydrogen) (Acids) (Bases (Chemistry))

5.3700

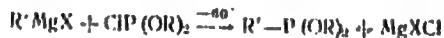
78081  
SOV/62-60-1-27/37

AUTHORS: Kabachnik, M. I., Tsvetkov, Ye. N.

TITLE: Brief Communications. Organolithium Compounds in Synthesis of Esters of Alkyl- and Arylphosphonous Acids

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1950, Nr 1, pp 133-134 (USSR)

ABSTRACT: M. I. Kabachnik and Ye. N. Tsvetkov (Dokl. AN SSSR 117, 817, 1957) worked out a method for the synthesis of esters of alkyl- and arylphosphonous acids, using organomagnesium compounds. At low temperatures (-60°) alkoxy groups of dialkylchlorophosphites practically do not react with organomagnesium compounds; a selective replacement of chlorine takes place:

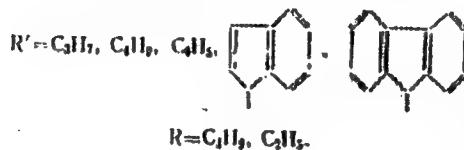
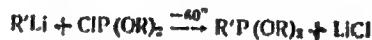


Card 1/3

Brief Communications. Organolithium  
Compounds in Synthesis of Esters of  
Alkyl- and Arylphosphorous Acids

78081  
SOV/62-60-1-27/37

This paper describes the synthesis of the above esters,  
using organolithium compounds instead of organomagnesium  
compounds:



It was shown that organolithium compounds can be used  
for the preparation of the above esters. The yield of  
esters obtained using organolithium compounds in some  
cases is higher than the yield of esters obtained using  
organomagnesium compounds. There are 7 references, 4  
U.S., 1 U.K., 2 Soviet. The U.S. and U.K. references

Card 2/3

5.3630

78088  
SOV/62-60-1-34/37

AUTHORS: Kabachnik, M. I., Shipov, A. E., Mastryukova, T. A.

TITLE: Letter to the Editor. Esters of Hypophosphorous Acid

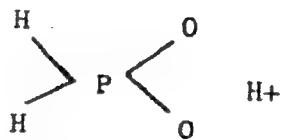
PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, Nr 1, p 146 (USSR)

ABSTRACT: The authors report that the following esters of hypophosphorous acid were obtained for the first time:  
 $(CH_3O)P(O)H_2$ , bp 25-25.5° (2.5 mm),  $n_{D}^{20}$  1.4275,  $d_{4}^{20}$  1.2177;  $(C_2H_5O)P(O)H_2$ , bp 31-32° (2 mm),  $n_{D}^{20}$  1.4250,  $d_{4}^{20}$  1.1120. They are colorless liquids, decompose easily at room temperature, become crystalline on cooling (about -20°), are stored at -60 to -70°. It is oxidized in air and hydrolyzed with water. Since hypophosphorous acid is very often considered to be an acid with a complex anion:

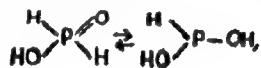
Card 1/3

Letter to the Editor. Esters of  
Hypophosphorous Acid

78088  
SOV/62-60-1-34/37



the existence of its esters was in doubt. On the other hand, A. I. Brodskiy and coworkers showed the presence of tautomerism:



which argued for the possibility of existence of its esters. It was found that hypophosphorous acid readily reacts (in the cold) with diazoalkanes to form esters, indicating that hypophosphorous acid has a covalent, not complex structure. The fact that only 1 mole of diazoalkane reacts with hypophosphorous acid (even in the presence of a large excess of diazoalkane) indicates

Card 2/3

5.3/00

81427  
S/030/60/000/06/04/043  
B004/B008

AUTHOR: Kabachnik, M. I., Academician

TITLE: Twofold Reactivity and Tautomerism<sup>1</sup>

PERIODICAL: *Vestnik Akademii nauk SSSR*, 1960, No. 6, pp. 52-60

TEXT: The author states in a short historical survey that twofold reactivity was wrongly identified with the conception of tautomerism. Papers by A. Ye. Chichibabin are mentioned among others in this connection. On the basis of papers by A. N. Nesmeyanov, R. Kh. Freydlina, A. Ye. Borisov, I. F. Lutsenko, V. A. Sazonova, and his own papers jointly with T. A. Mastryukova and S. T. Ioffe, the author explains next that twofold reactivity must not always be conditional on tautomerism. The action of conjugated single- and double bonds proved to be far more comprehensive, and a systematization of the linkages ( $n - \pi$ ,  $\sigma - \pi$ ,  $\pi - \sigma$  linkage etc., Scheme 6) was developed. Tautomerism only means a state of equilibrium between isomers. It may be the cause of twofold reactivity, but the latter may also be caused by more general causes like linkage of bonds.

Card 1/2

X

KABACHNIK, M.I.; IOFFE, S.T.; MASTRYUKOVA, T.A.

Tautomerism in aprotic media. Tautomeric equilibrium of phosphorus  
thio acids in benzene and chlorobenzene. Zhur. ob. khim. 30  
no.8:2763-2767 Ag '60. (MIRA 13:8)

1. Institut elementoorganicheskikh soyedineniy Akademii nauk  
SSSR.

(Tautomerism) (Phosphorus acids)

MASTRIUKOVA, T.A.; GFTER, Ye.L.; KAGAN, Yu.S.; PAYKIN, D.M.; SHABANOVA,  
M.P.; GAMPER, N.M.; YEFIMOVA, L.P.; KABACHEV, M.I.

Phosphoroorganic insecticides. 3-Chlorobutanyl-2-phosphates and  
thiophosphates. Zhur. ob. khim. 30 no.9:2813-2816 S '60.

(MIRA 13:9)

1. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR.  
(Insecticides)

S/079/60/030/010/011/030  
B001/B066

AUTHORS:

Kabachnik, M. I. and Tavetkov, Ye. N.

TITLE:

Esters of the Cyclopentadienyl-, Indenyl-1-, and  
Fluorenyl-9-phosphinic Acids

PERIODICAL:

Zhurnal obshchey khimii, 1960, Vol. 30, No. 10,  
pp. 3227 - 3233

TEXT: The authors were induced by the problem of the tautomerism of trivalent phosphorus compounds to synthesize cyclopentadienyl phosphinic acid esters, to investigate their properties, and to determine their structure. Two structures are possible for these compounds - the covalent one with a trivalent phosphorus atom (I), and the "ylide structure" having an aromatic cyclopentadienyl radical (IV). This structure may be formed as a result of the transition of the proton from the cyclopentadienyl ring to the trivalent phosphorus atom. Tautomeric transformations (I)  $\rightleftharpoons$  (IV) were assumed. To find out whether the formation of "ylide structures" is possible, also the corresponding derivatives of indene (V) and fluorene (VI) were investigated. The afore-mentioned compounds

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Esters of the Cyclopentadienyl-, Indenyl-1-, S/079/60/030/010/011/030  
and Fluorenyl-9-phosphinic Acids B001/B066

were synthesized by a method described in Refs. 4,5, by substituting different radicals for the chlorine atoms of the dialkyl chloro-phosphites in the reaction with organomagnesium and organolithium compounds at low temperatures. The dibutyl ester of cyclopentadienyl phosphinic acid (VII) was obtained by reacting cyclopentadienyl magnesium bromide with dibutyl chloro-phosphite at  $-60^{\circ}$ . The first investigation results of this compound already suggested the covalent structure, and not the "ylide" structure. The transformations of the above-mentioned ester (VII) (Schemes 1 and 2) confirm the opinion that the resultant phosphinic esters are derivatives of the trivalent phosphorus of covalent structure. The possibility of a tautomeric equilibrium which is shifted toward the covalent types will still have to be considered. This, however, must be proved experimentally. Thus, some chemical properties of cyclopentadienyl-, indenyl-1-, and fluorenyl-9-phosphinic acid esters were investigated; the transformations carried out suggest the presence of a trivalent phosphorus atom in the molecules of these compounds, as well as two double bonds in the ester of cyclopentadienyl phosphinic acid. The authors thank M. Ye. Movsesyan for taking the Raman spectra.

Card 2/3

5.3630

80087  
8/020/60/131/06/29/071  
B011/B005AUTHORS: Kabachnik, M. I., Academician, Tsvetkov, Ye. N., Chzhan Zhun-yuyTITLE: Esters of Unsaturated Phosphinous Acids

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 131, No. 6, pp. 1334 - 1337

TEXT: The authors described the synthesis and some transformations of the derivatives of vinyl-, ethinyl-, and p-vinylphenylphosphinous acids. The esters of the acids mentioned in the title have not yet been described in publications; they open the possibility of synthesizing various organophosphorus substances, including polymers. Dibutyl esters of vinyl- and ethinylphosphinous acids (Table 1, I and II) were obtained by the method of Ref. 1 (see Scheme). In a similar way, the butyl ester of secondary vinylphenylphosphinous acid (IV) was synthesized from vinylmagnesium bromide and phenylbutoxychlorophosphine (III). A styrene derivative (V) was produced from p-vinylphenylmagnesium chloride and diethylchlorophosphite. Complex formers - in this case pyridine (according to Ye. L. Gefter, Ref. 2) - must be used to extract the esters mentioned in the title. These esters are comparatively resistant to hydrolysis. Therefore, washing with water or sodium-bicarbonate solution can be used to decompose the

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Esters of Unsaturated Phosphinous Acids

800B7  
S/020/60/131/06/29/071  
B011/B005

complex compounds with magnesium halides. The esters produced oxidize easily in the air, but as it seems, less energetically than the corresponding alkylphosphinous esters. The authors confirmed the structure of (I) and (II) by some of their reactions; they are unsaturated derivatives of trivalent phosphorus. Complete esters of phosphinous acids yield corresponding acid esters of these acids by hydrolysis (Ref. 3). In a similar way, the authors obtained easily polymerizable monobutyl esters of these acids (VI) and (VII) by reaction with a theoretical amount of acidified water in dioxane. The trivalence of phosphorus in the ester (I) was confirmed by sulfur addition and Arbuzov's regrouping with methyl iodide. The following products were obtained: dibutyl ester of vinylthiophosphinous acid (VIII), or butyl ester of vinylmethylphosphinous acid (IX), respectively. Polymeric products were mainly obtained in the attempt of carrying out Arbuzov's regrouping of (I) by boiling in excess methyl iodide. Polymerization also occurred in acetonitrile at 0°. The desired result was obtained with the use of petroleum ether but only after 4 hours at 100-110°. (I) being dienophilic enters the reaction of the diene synthesis with cyclopentadiene, and forms the corresponding adduct - the dibutyl ester of bicyclo-(1,2,2)-hepten-2-yl-6-phosphinous acid (X). The latter contains one atom of trivalent phosphorus in the molecule. This was confirmed by sulfur

Card 2/3

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S.3630

2209

S/020/60/135/002/019/036  
B016/B052AUTHORS: Kabachnik, M. I., Academician, and Tsvetkov, Ye. N.TITLE: A New Method of Synthesizing Esters of Dialkyl Phosphinous AcidsPERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 2,  
pp. 323 - 326 X

TEXT: The authors report on their attempts to use their method of synthesizing esters of alkyl phosphinous acids from dialkylchloro phosphites (Ref.1) for the synthesis of esters of dialkyl phosphinous acids. The initial substances were the acid chlorides of Menashutkin (not described in the text), alkyl-dichloro phosphites, and the corresponding organo-magnesium compounds. The reaction took place in the presence of pyridine as a form complexing compound and showed satisfactory yields:

$2R\text{MgX} + \text{Cl}_2\text{POR}' \xrightarrow[-60^\circ\text{C}]{4\text{C}_5\text{H}_5\text{N}} R_2\text{POR}' + 2[\text{MgX Cl} \cdot 2\text{C}_5\text{H}_5\text{N}]$ . The yields decrease in the absence of pyridine which probably expels the esters of dialkyl phosphinous acids from complex compounds with magnesium halide.

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53700

2209, 1153, 1236

S/020/60/135/003/025/039  
B016/B054

- 860.1

AUTHORS: Kabachnik, M. I., Academician, Chzhan Zhun-yuy, and  
Tsvetkov, Ye. N.

**TITLE:** Method of Synthesizing Tertiary Vinyl Phosphines and Their Oxides

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 3,  
pp. 603 - 605

TEXT: The authors report on their method of synthesizing tertiary mono-vinyl phosphines and their oxides. They proceeded from esters of secondary phosphinous acids (Refs. 6,7). In reactions with organomagnesium compounds in ether or tetrahydrofuran, these esters exchange the alkoxyl groups for corresponding alkyl radicals or for the vinyl radical. Tertiary phosphines are formed:  $R'POR'' + R''MgX \longrightarrow R'R'PR'' + R''OMgX$ . The easily procurable dibutyl ester of vinyl phosphinous acid (Ref. 7) can be used for the same purpose; but the exchange of the two alkoxyl groups for alkyl radicals does not always take place with satisfactory yields. The authors also synthesized divinyl phenyl phosphine from phenyl-dichloro phosphine

Card 1/2

S/020/60/135/004/022/037  
B016/B062

AUTHORS: Kabachnik, M. I., Academician, Medved', T. Ya., and  
Polikarpov, Yu. M.

TITLE: Phosphine Oxides Containing the Vinyl Group at the Phosphorus Atom

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 4, pp. 849-852

TEXT: The authors synthetized three vinyl phosphine oxides. The following reaction scheme is given:

$$\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{P}=\text{CH}-\text{CH}_2; \end{array}$$
 and 
$$\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{P}=\text{CH}-\text{CH}_2; \end{array}$$
 and 
$$\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{P}=\text{CH}-\text{CH}_2. \end{array}$$
 They contain the  
vinyl group directly at the phosphorus atom and have hitherto not been  
described. The authors used the addition reaction of ethylene oxide to  
phosphorus trichloride (described by M. I. Kabachnik and P. A. Rossiyskaya,  
Ref. 2) in the production of the  $\beta$ -chloro-ethyl ester of the diethyl  
phosphinous acid from diethyl-chloro phosphine, thus confirming the vali-

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Phosphine Oxides Containing the Vinyl Group  
at the Phosphorus Atom

S/020/60/135/004/022/037  
B016/B062

dity of this reaction for compounds of the type  $\text{PCl}_3$ ,  $\text{RPCl}_2$ , and  $\text{R}_2\text{PCl}$ . They proved that the  $\beta$ -chloro-ethyl ester of diethyl phosphinous acid is, when heated, converted into compounds of pentavalent phosphorus. The authors succeeded in isolating the two products of the regrouping of Arbuzov (not explained in the text) at the same time: a)  $\beta$ -chloro-ethyl diethyl phosphine oxide, and b) tetraethyl ethylene diphosphine dioxide. The authors assume here the same conversion mechanism as with the aromatic esters of phosphorous acid (Ref. 8): a) an intra- or intermolecular isomerization of the  $\beta$ -chloro-ethyl ester of diethyl phosphinous acid; b) the resulting  $\beta$ -chloro-ethyl diethyl phosphine oxide reacts in the way of halogen alkyls with the second molecule of the  $\beta$ -chloro-ethyl ester of diethyl phosphinous acid according to the scheme of the Arbuzov regrouping. The authors dehydrochlorinated the  $\beta$ -chloro-ethyl diethyl phosphine in a sealed tube by heating with triethyl amine. It is stated that diethyl-vinyl phosphine oxide is more conveniently obtained directly from the  $\beta$ -chloro-ethyl ester of diethyl phosphinous acid without isolating the intermediate product  $\beta$ -chloro-ethyl diethyl phosphine oxide. Analogously, the authors obtained dipropylvinyl phosphine oxide and ethylphenylvinyl phosphine

Card 2/7

KABACHNIK, M. I., YAKOVLEV, V. I., VOLKOVA, R. I., VODOVIK, N. N.,  
MAJAZANIK, L. ?, MASTRYUKOVA, T. A., ROZIKOVA, YE. K., FRUTENOV, N. K.,  
NIKHELSON, M. YA. (USSR)

"The Significance of Oxic Group and of its Position in an  
Anti-Cholinesterase Substance Molecule for its Inter-action  
with Cholinesterases and for Pharmacologic Effects."

Report presented at the 5th International Biochemistry Congress,  
Moscow, 10-16 August 1961

S/191/61/000/001/013/015  
B101/B205

AUTHORS: Gefter, Ye. L., Kabachnik, M. I.

TITLE: Synthesis of  $\beta$ -chloroethyl phosphinic acid dichloride

PERIODICAL: Plasticheskiye massy, no. 1, 1961, 63-65

TEXT: The conventional methods of synthesizing  $\beta$ -chloroethyl phosphinic acid dichloride - starting material for the synthesis of chlorides and esters of vinyl phosphinic acid - have the following disadvantages:

a) Treatment of di- $\beta$ ,  $\beta'$ -chloroethyl ester of  $\beta$ -chloroethyl phosphinic acid or of the isomerization products of tri- $\beta$ ,  $\beta'$ ,  $\beta''$ -chloroethyl phosphite (commercial chloroethyl phosphinic acid) with  $PCl_5$  at 150-160°C requires the application of pressure to warrant a yield of 70%. b) Interaction of  $PCl_3$ ,  $C_2H_4Cl_2$ , and  $AlCl_3$ , and subsequent hydrolysis is a very complicated procedure. c) Reaction of  $PCl_3$  with  $C_2H_4$  and  $O_2$  gives only low yields.

For this reason, the authors examined the possibility of obtaining sufficiently large yields of  $\beta$ -chloroethyl phosphinic acid dichloride

Card 1/3

S/191/61/000/001/013/015  
B101/B205Synthesis of  $\beta$ -chloroethyl...

without applying pressure. Two ways of this synthesis were studied: 1) Direct conversion of the di- $\beta$ , $\beta'$ -chloroethyl ester of  $\beta$ -chloroethyl phosphinic acid into the acid, and subsequent treatment with reagents leading to the formation of the acid chloride; 2) direct conversion of the  $\beta$ , $\beta'$ -chloroethyl ester of  $\beta$ -chloroethyl phosphinic acid (CEPA) into the acid chloride without synthesizing the free acid. Concerning 1) the following is noted: Pure or commercial di- $\beta$ , $\beta'$ -chloroethyl ester of CEPA may be converted into CEPA by reaction with anhydrous HCl at 140-160°C if atmospheric moisture is excluded:

$$\text{ClC}_2\text{H}_4\text{PO}(\text{OC}_2\text{H}_4\text{Cl})_2 + 2\text{HCl} \rightarrow \text{ClC}_2\text{H}_4\text{PO}(\text{OH})_2 + 2\text{Cl}_2\text{C}_2\text{H}_4$$

Treatment of this acid with thionyl chloride, phosgene,  $\text{PCl}_3$ , or  $\text{SiCl}_4$  failed. Treatment with  $\text{SOCl}_2$  in the presence of catalytic quantities of pyridine gave only a small yield of the acid dichloride. Treatment with  $\text{PCl}_5$  or  $\text{PCl}_3 + \text{Cl}_2$ , however, gave the dichloride of CEPA in yields of up to 80%. The second synthesis was brought about by interaction of  $\text{PCl}_5$  with the initial ester at 140-150°C, in the presence of small amounts of metallic chlorides

Card 2/3

Synthesis of  $\beta$ -chloroethyl...

S/191/61/000/001/013/015  
B101/B205

( $\text{FeCl}_3$ ,  $\text{CuCl}_2$ , or  $\text{AlCl}_3$ ) as catalysts; reaction with  $\text{SiCl}_4$ ,  $\text{COCl}_2$ ,  $\text{PCl}_3$ , or  $\text{SOCl}_2$ , however, failed. Exclusion of atmospheric moisture and stepwise addition of  $\text{PCl}_5$  are needed to obtain a yield of 80%. When using tri- $\beta, \beta', \beta''$ -ethyl phosphite, the yield varied from 65 to 70%. The synthesis failed when using  $\text{PCl}_3 + \text{Cl}_2$  because of the formation of yellow phosphorus. L. S. Lumentsova assisted in the experiments. There are 9 references; 6 Soviet-bloc and 2 non-Soviet-bloc.

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Card 3/3

VOLKOVA, R.I.; GODOVIKOV, N.N.; KABACHNIK, M.I.; MAGAZANIK, L.G.;  
MASTRYUKOVA, T.A.; MIKHAIL'SON, M.Ya.; ROZHKOVA, Ye.K.;  
FRUYENTOV, N.K.; YAKOVLEV, V.A.

Chemical structure and biological activity of phosphorus  
organic cholinesterase inhibitors. Vop. med. khim. 7 no.3:  
250-259 Ny-Je '61. (MIRA 15:3)

1. Laboratory for the Pharmacology and Biochemistry of  
Biologically Active Compounds, "I.M. Sechenov" Institute of  
Evolutionary Physiology, Academy of Sciences of the U.S.S.R.,  
and Laboratory of Organophosphorus, Institute of Elementoorganic  
Compounds, Academy of Sciences of the U.S.S.R., Leningrad.

(CHOLINESTERASES)  
(PHOSPHORUS ORGANIC COMPOUNDS)

89908

53630

2209, 1287, 1153

S/062/61/000/002/004/012  
B115/B207

AUTHORS:

Medved', T. Ya. and Kabachnik, M. I.

TITLE:

Organophosphorus monomers. Report no. 2.  $\alpha$ -Chloro-  
and  $\alpha$ -bromo vinyl phosphonic acids and their derivatives

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh  
nauk, no. 2, 1961, 270-274

TEXT: In their previous paper, the authors proved that the dichloride of vinyl phosphonic acid  $\text{CH}_2 = \text{CHPOCl}_2$  can be easily obtained by catalytic dehydrochlorination of  $\beta$ -chloro ethyl phosphonic acid dichloride. This paper gives the results of bromination and chlorination of vinyl phosphonic acid dichloride. The addition of bromine to vinyl phosphonic acid dichloride is simple, and occurs within 24 hr if an equimolar mixture of the acid chloride and bromine are left standing in chloroform solution at room temperature.  $\text{CH}_2 = \text{CHPOCl}_2 + \text{Br}_2 \rightarrow \text{BrCH}_2\text{CHBrPOCl}_2$ . Thus, the  $\alpha, \beta$ -dibromo ethyl phosphonic acid dichloride was obtained, and hydrolyzed to the free acid.

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S/062/61/000/002/004/012  
B115/B207

Organophosphorus monomers. Report ...

The aniline salt of this acid melts at 194-195°C. While the authors tried to obtain an anilide of this acid, a dehydrobromination occurred, and a dianilide of  $\alpha$ -bromo vinyl phosphonic acid was separated. In the dehydrobromination of  $\alpha, \beta$ -dibromo ethyl phosphonic acid dichloride:

$\text{BrCH}_2\text{CHBrPOCl}_2 \xrightarrow[-\text{HBr}]{\text{BaCl}_2} \text{CH}_2=\text{CHBrPOCl}_2$ , the acid chloride of  $\alpha$ -bromo vinyl phosphonic acid forms in a yield of approximately 80%. The free acid, a colorless syrup, was obtained by hydrolysis of  $\alpha$ -bromo vinyl phosphonic acid. The aniline salt of this acid melts at 187-188°C. Together with alcohol, the chloride of  $\alpha$ -bromo vinyl phosphonic acid yielded the ethyl ester whose structure was determined by ozonization. A dimedone derivative of formaldehyde was obtained from the distillate. The vinyl phosphonic acid dichloride reacts with bromine more readily than with chlorine. At room temperature, chlorine adds very slowly to the acid chloride. Sunlight accelerates the reaction somewhat. Reaction products are obtained in an 80% yield by heating the reaction mixture in sealed tubes to 125-130°C within 5 hr. This process entails,

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Organophosphorus monomers. Report ...

apart from the addition of chlorine to the double bond, and the formation of  $\alpha, \beta$ -dichloro ethyl phosphonic acid dichloride, a separation of hydrogen chloride and simultaneous formation of  $\alpha$ -chloro vinyl phosphonic acid dichloride. The two acid chlorides were obtained in pure form. On the basis of published data, the authors tried to prepare the  $\alpha, \beta$ -dichloro ethyl phosphonic acid dichloride by oxidizing phosphorylation of vinyl chloride. They obtained a mixture of unseparable isomers. It was, however, possible to convert this acid by catalytic dehydrochlorination over barium chloride into the dichloride of  $\alpha$ -chloro vinyl phosphonic acid. Moreover, it was possible to dehydrochlorinate it also without a catalyst and at lower temperature. When the reaction mixture resulting from the chlorination of the vinyl phosphonic acid dichloride was left standing at 150-155°C before distillation until no hydrogen chloride was separated any more, the chief product obtained was  $\alpha$ -chloro vinyl phosphonic acid dichloride, beside a small quantity of  $\alpha, \beta$ -dichloro ethyl phosphonic acid dichloride. About the same result was obtained when heating the reaction mixture to 140-150°C. Methyl- and ethyl esters of  $\alpha$ -chloro

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S/062/61/000/002/004/012  
B115/B207

Organophosphorus monomers. Report ...

vinyl phosphonic acid were obtained from the reaction of  $\alpha$ -chloro vinyl phosphonic acid dichloride with alcohols. By interaction of the ethyl ester with aniline, the dianilide of this acid was obtained. In conclusion, the authors find that dichlorides of  $\alpha$ -bromo- or  $\alpha$ -chloro vinyl phosphonic acid can be easily obtained by way of adding bromine or chlorine to the vinyl phosphonic acid dichloride with subsequent dehydrohalogenation of the reaction products. There are 4 Soviet-bloc references.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds of the Academy of Sciences USSR)

SUBMITTED: November 25, 1959

Card 4/4

22515

S/062/61/000/004/004/008  
B118/B208

15.8114 2209

4

AUTHORS: Kabachnik, M. I. and Medved', T. Ya.

TITLE: Organophosphorus monomers. 3. Vinyl thiophosphinic acid and some of its derivatives

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, no. 4, 1961, 604-608

TEXT: The present paper reports on the synthesis of the dichloride and some derivatives of vinyl thiophosphinic acid. The dichloride of  $\beta$ -chloroethyl thiophosphinic acid was synthesized by reacting the dichloride of  $\beta$ -chloroethyl phosphinic acid with  $P_2S_5$  according to the reaction of M. I. Kabachnik and N. N. Godovikov:  
$$5ClCH_2CH_2POCl_2 + P_2S_5 \longrightarrow 5ClCH_2CH_2PSCl_2 + P_2O_5$$
 (I). This acid dichloride (I) gives with triethylamine (or other bases) in ether solution the dichloride of vinyl thiophosphinic acid (II):  
$$ClCH_2CH_2PSCl_2 + (C_2H_5)_3N \longrightarrow CH_2-CHPSCl_2 + (C_2H_5)_3N \cdot HCl$$
 (II). Vinyl

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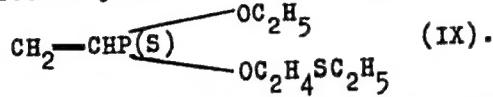
22515

S/062/61/000/004/004/008  
B118/B208

Organophosphorus monomers. ...

thiophosphinic acid (III) obtained by hydrolysis of the acid dichloride is sirupy. Its aniline salt melts at 105-106° with decomposition. The acid dichloride (II) gives with aniline the dianilide of the acid  $\text{CH}_2=\text{CH}-\overset{\text{S}}{\text{P}}=(\text{NH}_2\text{C}_6\text{H}_5)_2$  (V). By reacting the dichloride (II) with

2 molecules methyl alcohol in the presence of 2 molecules  $(\text{C}_2\text{H}_5)_3\text{N}$  the dimethyl ester of the acid  $\text{CH}_2=\text{CHPS}(\text{OCH}_3)_2$  (VI) results. Application of only one mole alcohol and one mole base gives the compound  $\text{CH}_2=\text{CHP}(\text{S})(\text{OC}_2\text{H}_5)\text{Cl}$  (VIII). Further reaction of the latter with a second alcohol molecule yielded the complete esters, e.g., the ester



This ester and esters of the same type add secondary amines giving, e.g., the compounds  $\text{R}_2\text{NCH}_2\text{CH}_2\text{P}(\text{S})(\text{OC}_2\text{H}_5)(\text{OC}_2\text{H}_4\text{SC}_2\text{H}_5)$  ( $\text{R}=\text{CH}_3$  (X) and  $\text{C}_2\text{H}_5$  (XI)). Compound (IX) isomerizes at 135° within 8 hr to the ester

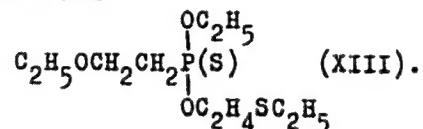
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22515

S/062/61/000/004/004/008  
B118/B208

Organophosphorus monomers. ...

$\text{CH}_2-\text{CHPO}(\text{OC}_2\text{H}_5)(\text{SC}_2\text{H}_4\text{SC}_2\text{H}_5)$  (XII); compound (IX) (as well as its isomerization product (XII)) add an alcohol molecule, when heated with alcohol in the presence of sodium methylate, and form the corresponding ester of ethoxy-ethyl thiophosphinic acid



The ethoxy group presumably enters the  $\beta$ -position. There are 3 Soviet-bloc references.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds, Academy of Sciences USSR)

SUBMITTED: January 21, 1960

Card 3/3

KABACHNIK, M.I.; GILYAROV, V.A.

Imides of phosphorus acids. Report No.5: Reactions of trialkyl-phosphites with hydrazoic acid. Izv.AN SSSR.Otd.khim.nauk no.5: 816-818 My '61. (MIRA 14:5)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.  
(Phosphorous acid) (Hydrazoic acid)